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AN INVESTIGATION OF ELECTRODEPOSITED ALLOYS FOR
PROTECTION OF STEEL AIRCRAFT PARTS

A. B. TAYLOR, JR.
J. E. BRIDE
J. A. GURKLIS
C. L. FAUST

BATTELLE MEMORIAL INSTITUTE

**AN INVESTIGATION OF ELECTRODEPOSITED ALLOYS FOR
PROTECTION OF STEEL AIRCRAFT PARTS**

*A. B. Tripler, Jr.
J. E. Bride
J. A. Gurklis
C. L. Faust*

Battelle Memorial Institute

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FOREWORD

This report was prepared by the Battelle Memorial Institute under Contract No. AF 33 (038) 8750 identified by Research and Development Order No. 611-11, "Electrodeposition and Electrochemical Treatments." It was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. C. E. Foertmeyer acting as project engineer. The report is one of a series to be published on the project as research progresses. The work covered by this report dates from 5 Nov 1949 to 15 Feb 1951.

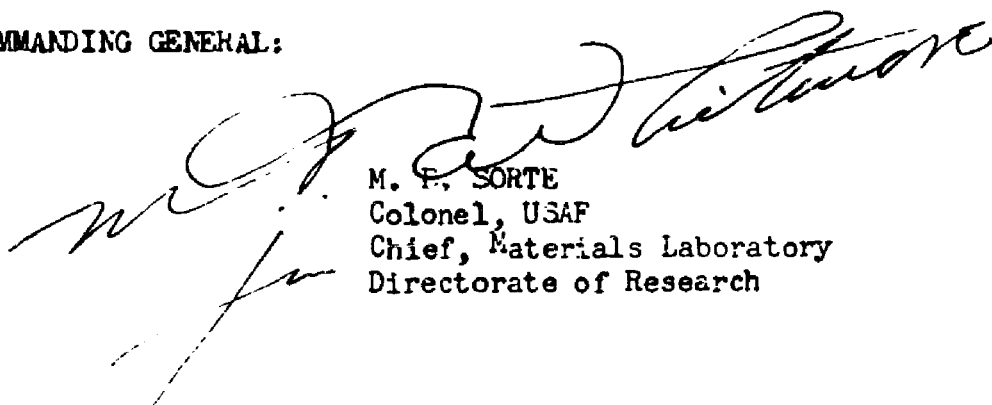
ABSTRACT

Work done in this report covers the preparation and evaluation of eleven alloy deposits. Methods and solutions used for the preparation of both co-deposits and diffused coatings are listed. Results of "Wet-Dry" exposure tests, x-ray diffraction, potential - time data of various coatings have been tabulated. A graphical system for the better interpretation and rating of the "Wet-Dry" test was developed. Mangarese-zinc alloy diffusion type coatings of 50% mangarese and 50% zinc composition exhibited the most promising corrosion protection properties of the various coatings investigated. Seventy-two panels were prepared and are being tested in outdoor exposure in northern Florida in order to evaluate the corrosion protection afforded by mangarese and mangarese-zinc coatings as compared to zinc, zinc chromated, and cadmium coatings. It is believed that a co-deposited zinc-silver coating of 25% silver merits further investigation. Also further studies of corrosion products should yield information enabling the design of an alloy coating of maximum protection.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDING GENERAL:



M. F. SORTE
Colonel, USAF
Chief, Materials Laboratory
Directorate of Research

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OBJECTIVES FOR THE PROJECT

The ultimate objective is to develop electrodeposited coatings which will provide better protection for aircraft steel parts than does zinc or cadmium plate, particularly in tropical regions.

Two years have been spent in partial attainment of this objective, and the results have been reported. (See Final Report, dated November 30, 1947, and Final Report, dated June 28, 1949).

Under the present contract, the objectives were:

- (1) Continuation of work on zinc-silver, zinc-lead, and zinc-tin alloy platings.
- (2) Measurement of electrode potentials of manganese-tin, manganese-zinc, and manganese-copper alloys in 3% sodium chloride solution, distilled water, and CO₂-saturated water. This assumed that the alloys would be electrodeposited. Any of the alloys showing favorable potentials were to be exposed in the "wet-dry" cabinet. (The manganese-nickel system is also included here, insofar as the plating investigation is concerned. Potential measurements on cast manganese-nickel alloys had been completed.)
- (3) Investigation of methods for obtaining good adhesion of aluminum deposits on steel, using aluminum-plating methods which had already been developed.
- (4) Investigation of methods for depositing zinc-chromium, cadmium-chromium, and cadmium-manganese alloys. Those which could be deposited and show favorable potentials were to be exposed in the "wet-dry" test.
- (5) Outdoor exposure of alloy coatings which show good corrosion resistance in the preliminary tests. This was to be done at the Battelle North Florida Research Exposure Station, if, and as, time permitted during the contract period.

- (6) Investigation of other pure metals or alloys showing promise as substitutes for zinc and cadmium. The only metal in this category is molybdenum. Its potential is such that it would have to be alloyed with zinc, cadmium, or manganese.

INTRODUCTION

The experimental approach used in attaining the foregoing objectives was somewhat different than visualized for the project at the start.

After a time it became apparent that codeposition studies were consuming too much time in proportion to the benefits derived, and that preparation of alloy coatings on steel would probably be expedited by using diffusion methods. For this reason, much of the effort was centered on obtaining alloy coatings by diffusion heat treatments of alternate layers of pure-metal plates.

Less emphasis was placed on potential measurements. Where the coatings were readily prepared, it was thought better to test them immediately in the "wet-dry" cabinet. Potential and current-density measurements were used extensively during the first and second years of work and were useful in separating good prospects from the poor ones. It will be recalled, however, that in the early work, cast alloy specimens, rather than coatings, were used.

Methods for depositing aluminum from nonaqueous organic solutions were developed here on a project sponsored by the Navy. A

study of methods for improving the adhesion of aluminum to steel was planned. This study was contingent upon the Navy's continuing the project, but the project was closed. The amount of effort for continuing the work under this project would have been greater than that allotted in view of the other lines of investigation that had to be carried on. For this reason, the investigation of aluminum plate adherence was not begun.

This report is a Final Report in the sense that it represents the completion of a phase of an overall investigation. The work to be accomplished during this phase was set forth in the contract which authorized this project. Recently a supplemental contract has been entered into, which authorizes outdoor testing of protective coatings described later in this report, and an investigation of methods for electrodeposition of certain binary manganese alloys.

RESULTS ACCOMPLISHED

An alloy coating containing 50% manganese and 50% zinc shows promise as a protective material for steel*. This alloy is superior to pure zinc as a protective coating when exposed in the "wet-dry" cabinet**. The coating was prepared by heat treating a duplex coating of manganese and zinc electroplates so as to cause interdiffusion. The alloy has an advantage over pure manganese in that the corrosion products appear to be less bulky and are more adherent.

*Most plated panels discussed herein had an S.A.E. 4130 steel basis for plating, as shown in Appendix I.

** See Appendix I for description.

Manganese and tin were codeposited from a tartrate-oxalate bath, but the reproducibility in plate composition was poor. The study of manganese-tin alloys containing 40% to 60% manganese was continued with diffusion coatings. These alloys showed better inherent corrosion resistance than pure manganese, since the characteristic brown corrosion products developed more slowly on the alloy. Pure manganese gave a higher degree of sacrificial protection.

A peculiar phenomenon was observed with the manganese-tin diffusion alloys. After standing at room temperature for five or more days, a gray powder formed on the surface. X-ray diffraction tests showed that the powder was tin, but not gray tin. No explanation was found for this apparent "disintegration" of the diffusion alloy.

Attempts were made to prepare a sound codeposit of zinc and silver, first using an iodide solution, and second using a thiosulfate solution. Both zinc and silver were found in the deposit which was powdery and nonadherent.

Zinc-silver alloy coatings prepared by diffusion showed extremely poor resistance in the "wet-dry" test. This is thought to be due to a small amount of free silver in the coating. It is believed that, if the coating can be prepared so as to eliminate the free silver, a resistant coating will result in accordance with expectations from the potential measurements and weight-loss measurements on cast zinc-silver alloys.

Codeposits of manganese and nickel were obtained from solutions containing ammonium salts. The manganese content was very low, however.

Some evidence of diffusion was found after heat treating manganese and nickel duplex plates. After a twenty-one-hour heat treatment, the identification of pure nickel and pure manganese was questionable and a strong pattern of iron and an unknown phase was found.

Slight evidence of the interdiffusion of zinc and chromium electroplates was found. The only X-ray data available were obtained here from some low-chromium castings. The lack of complete X-ray data was a handicap.

No interdiffusion was detected of cadmium and chromium or of manganese and cadmium electroplates.

No work was done on manganese-copper alloys, because it had been mutually agreed to defer this until the Navy tests on the same subject were complete.

Work supported at Battelle by the Tin Research Institute, Inc., overcame previous difficulties with zinc-tin alloy plating. Revised directions for using the zinc-tin bath are given in Appendix I.

Experiments on the codeposition of zinc and lead resulted in non-adherent, coarsely crystalline deposits containing mostly lead.

Zinc-nickel-coated ("corroized") 4130 steel panels were exposed in the "wet-dry" test, in which they rusted fairly rapidly. As the nickel content increased from 25% to 50%, the advance of rusting became slower.

Cadmium-tin diffusion coatings, and also cadmium-tin codeposited coatings (both types containing about 50% cadmium) were exposed in the "wet-dry" cabinet. These coatings are comparable to pure cadmium coatings, with the codeposited alloy being somewhat better.

Cadmium-silver codeposited coatings rusted early in the "wet-dry" test, but subsequent rusting progressed slowly. This alloy was slightly inferior to pure cadmium in the "wet-dry" test. Weight-loss measurements on cast cadmium-silver specimens, after exposure in the "wet-dry" test, showed the alloy to have about the same resistance as pure cadmium.

Although one of the requisites for a substitute coating was that it give sacrificial protection, some thought was given to the non-sacrificial type of coating. An iron-chromium alloy containing 6% iron has been developed here (under a separate government sponsorship). The alloy plate does not have the usual cracks associated with chromium deposits. Because the coating could conceivably give envelope-type protection, it was tested in the "wet-dry" cabinet. The iron-chromium alloy, however, was no better than the chromium-plated panels which were exposed at the same time.

The effect of light nitriding of the steel surface prior to pure zinc plating was studied. The nitrided panels showed no significant improvement over the unnitrided panels.

A proposed graphical system for rating coatings after exposure in the "wet-dry" test is described. The method involves a graphical integration of time and extent of corrosion. It represents a first attempt to obtain a single number which describes the relative corrosion resistance.

The manganese-zinc corrosion products were studied by means of X-ray diffraction. Only manganese oxides were detected. The type of oxide appears to be related to the composition of the alloy.

Seventy-two coated 4130 steel panels, for outdoor exposure at the Battelle North Florida Research Station, were prepared. Pure manganese, manganese-zinc, and zinc-tin coatings will be tested in comparison with pure zinc, zinc plus chromate, and pure cadmium. Three thicknesses, 0.1 mil, 0.3 mil, and 0.5 mil, were prepared for each type of coating.

DISCUSSION OF ESSENTIAL DATA

Zinc-Silver Alloy Coatings

Introduction

Measurement of dynamic potentials and corrosion-current density of cast alloys previously had shown that a zinc-silver alloy containing 25% silver held promise for improved corrosion resistance in comparison with pure zinc. (See Final Report, dated June 28, 1949.) This was further substantiated by weight-loss measurements on cast alloy specimens exposed in the "wet-dry" cabinet. The 25% silver alloy lost less weight in the test than either zinc or cadmium. (See Final Report, dated June 28, 1949.) Experiments were then started on the preparation of alloy coatings by electrodeposition.

Experiments on the Codeposition of Zinc and Silver

These experiments were started during the second year of work on this project. According to calculations (see Final Report dated June 23, 1949), the deposition potentials of zinc and silver could be brought closer together by complexing the silver as a complex iodide.

This would reduce the silver ion concentration, making its deposition potential more negative*. By using a high concentration of zinc iodide (which does not form a complex in iodide solutions), the zinc deposition potential would become somewhat more positive.

Potential measurements in solutions containing the single ions, zinc or silver, demonstrated that such a change took place. Even with the small amount of polarization, due to passage of current, the deposition potentials were not close enough so that codeposition could be predicted.

When the ions were present in the same solution, codeposition did occur, possibly indicating increased polarization of the silver. The codeposition experiments are described in Table 20, Appendix I.

In general, the codeposits from the iodide solutions were characterized by a rough and powdery surface. The deposits were not rough from the very beginning. A thin flash-plate was obtained before the roughness would begin. Raub and Mulhorst**, using a cyanide solution, and Wood and Saunders***, using a cyanide-hydrazide solution, also were able to get only flash plates, followed by increasing roughness.

A number of additional agents were tried without improving the deposit. (See Table 20, Appendix I.)

*The convention as to the sign of the potential is the one adopted by the Electrochemical Society, where the active end of the electromotive-force series is negative.

**Metallforschung 2, 33 (1947).

"A Study of Silver-Zinc Coatings for Steel Flatware", Report to War Metallurgy Board, March 1, 1943.

The first experiments were run at 85°F. Increasing the temperature to 177°F. caused the deposit to become worse. Lowering the temperature to 40°F. seemed to improve the deposits, but they still were not acceptable as coatings.

The plate composition is quite sensitive to current density. Figure 1 shows this relationship.

The powdery deposits were at first believed due to a silver immersion plate which formed after the initial deposit of alloy. The alloy, being more active than silver, displaces silver from the solution. This view has been discarded and for reasons discussed later in this section.

Because of the thought that immersion plating was responsible for the poor deposits, new complexing agents were sought.

The first of these was the silver ethylene thiourea complex. The complex is easily formed from ethylene thiourea and silver nitrate. It is soluble in water and silver deposits were obtained at 15 amps./sq.ft. and 80°F. Static-potential measurements in this solution resulted in values about 200 millivolts more electropositive than those in iodide solutions. This indicated that the silver was not complexed enough to obtain the desired shift in deposition potential.

Pyridine showed insufficient power as a complexing agent. Silver in pyridine was oxidized to a divalent form by persulfate, but this complex was also weak, the silver being displaced easily.

During an investigation for another sponsor, it was found that, if a solution of silver nitrate in dry acetonitrile was treated with dry ammonia gas, a precipitate formed which was presumably a silver

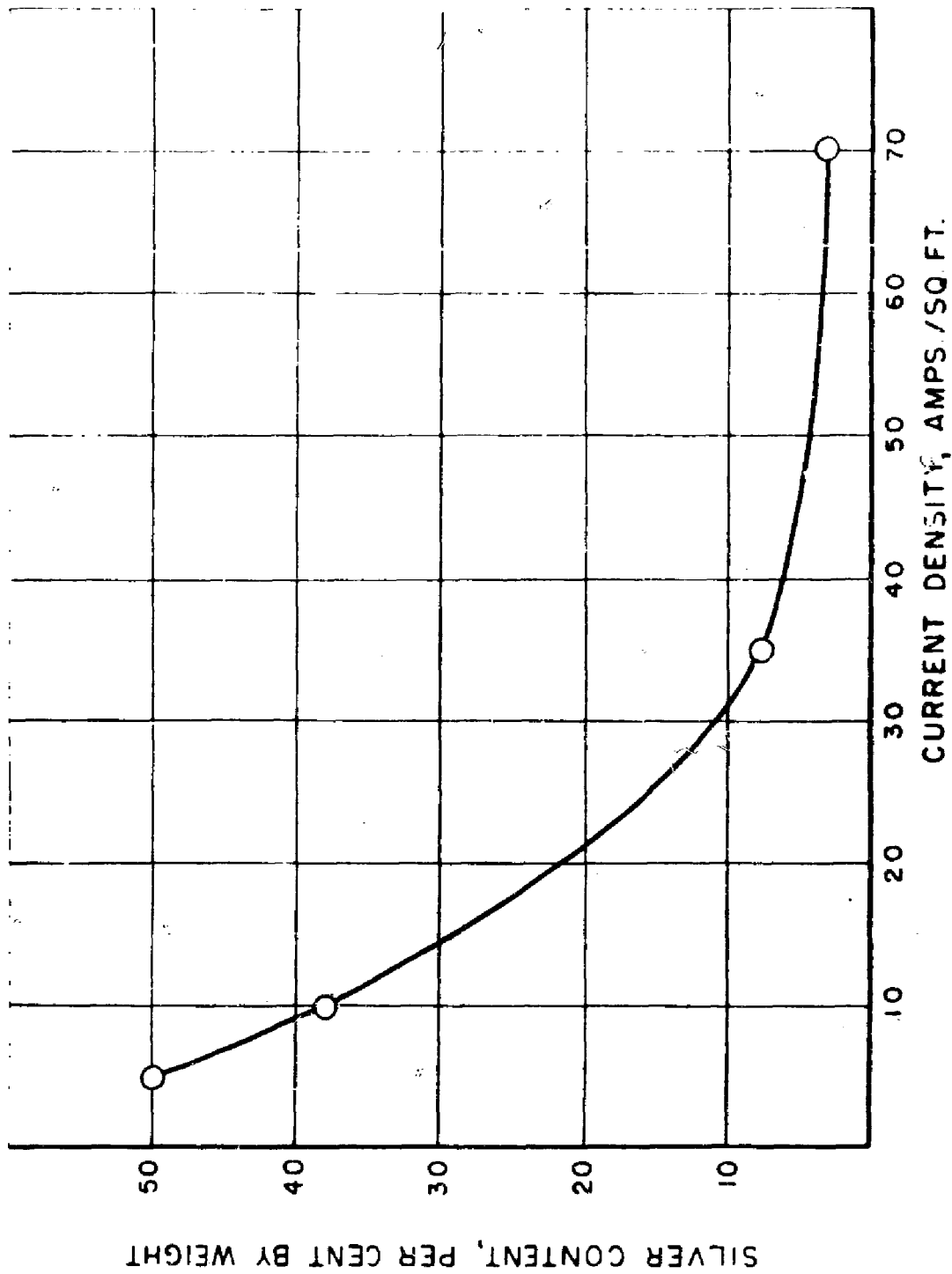


FIGURE 1. EFFECT OF CURRENT DENSITY ON SILVER CONTENT OF ZINC-SILVER DEPOSITS FROM THE IODIDE SOLUTION

complex. The solution was then saturated with respect to this silver complex. Zinc did not displace silver from such a solution as long as no water was present. A deposit of black colloidal silver was obtained on passage of a current. This solution did not appear to hold practical possibilities and the investigation was discontinued.

Static-potential measurements on the silver thiosulfate complex indicated it to be only slightly less favorable than the iodide complex, being 20 millivolts less negative. With a current of one amp./sq.ft., silver sulfide was produced at the cathode and the cathode-potential value changed from -0.414 volts to -1.10 volts. This large change in potential resulted from the great reduction of silver ions adjacent to the cathode when the silver precipitated as Ag_2S (the equilibrium constant for Ag_2S is 1.0×10^{-51}). A study of the literature revealed that if certain precautions were taken the precipitation could be avoided. Hickman*, et al., defined the conditions.

Hickman recommended that the solution be acidic, that sulfite and gelatin be present, and that rapid agitation be used. The directions were followed in solutions containing both zinc and silver. Spongy nonadherent deposits containing both silver and zinc resulted. Sulfur was also found in the deposit, although less of it deposits if gelatin is present.

During these experiments, silver was easily displaced by a more active metal, such as zinc, from a thiosulfate complex, but if zinc is present no displacement occurred. On electrolyzing the solution, an unsatisfactory deposit resulted. This cast doubt on the earlier

*Ind. Eng. Chem., 25, 202 (1933).

observation that the poor zinc-silver deposits were probably caused by a simultaneous immersion deposit. Another factor which made the immersion theory untenable is that increasing the current density did not improve the deposits.

Because of time limitations and the desirability of producing a satisfactory zinc-silver alloy coating within the contract period, the electrodeposition work was discontinued in favor of preparation by diffusion. This decision applied not only to the zinc-silver alloys, but wherever this method of preparation was practicable and could save time in studying other alloy coatings.

Experiments on Zinc-Silver Alloy Coatings by Diffusion

In general, the preparation of alloy coatings by diffusion consisted of plating Metal A on the steel panels, plating Metal B over Metal A, thus forming a duplex plate, and then heating them to a sufficiently high temperature that interdiffusion occurred. The alloy composition was controlled by the relative amounts of A and B which were deposited. The heat treating can be done in an inert-gas atmosphere, in air, or in an oil bath. The choice depended on the temperature and the chemical properties of the metals.

The initial experiments with duplex plates of zinc and silver disclosed that interdiffusion of zinc and silver took place at 700°F., in a purified-nitrogen atmosphere to prevent oxidation. The extent of diffusion was determined, in these early experiments, by microexamination. Subsequent use of X-ray diffraction for examination of the diffusion

specimens expedited the work, because relatively thin coatings could be used (0.3 mil, as compared with 2 to 4 mils for microexamination), and the specimens required no special preparation, such as was necessary for microexamination. Experiments with duplex plates with a total thickness of 0.3 mil demonstrated that diffusion could be brought about in one hour at 500°F.

At first it appeared best, in preparing the duplex deposits, to plate the silver directly on the steel and then zinc plate. Silver does not diffuse into steel at temperatures (500°F.-800°F.) which cause interdiffusion of zinc and silver. There was a possibility that zinc would, if deposited first, diffuse into the steel. Thus, a zinc-silver alloy coating low in zinc would result. If sufficient zinc was "robbed" by the steel, the coating might not provide sacrificial protection for the steel.

However, when silver was plated directly on the steel (using a single strike solution and a regular plating bath, but no special pre-treatment), it blistered during heat treatment. Therefore, duplex coatings were prepared with the zinc next to the steel. The total thickness was 0.0003 inch (the thickness previously chosen as standard for the "wet-dry" exposure test), and the respective weights were such as to give a resultant alloy of 25% silver content. The coatings were heat treated in a purified-nitrogen atmosphere for one hour at 500°F. Observation of the coatings, following heat treatment, showed them to have changed in color from silvery white to a blue gray. This alone was indicative of diffusion having taken place. The coating was wrinkled along the edges of the specimens but no breaks were apparent.

X-ray diffraction measurements showed the desired epsilon phase (see constitution diagram, p. 1155, American Society for Metals Handbook, 1943) to be present and also a small amount of free silver (estimated to be, at most, a few per cent).

The static potential of one of the specimens was measured in three per cent sodium chloride solution. The values are given in Table 1. The results show that diffusion took place. If diffusion had not taken place or had been incomplete, the potentials would have been more electropositive.

The value for 60 minutes is some hundred millivolts more negative than that for the cast alloys of the same composition. (See Final Report dated November 30, 1947, p. 45.) At 120 minutes and beyond, the potential is equal to that of the cast alloy.

After 330 minutes in the salt solution, the panel showed only a trace of corrosion products. The coating flaked at the edges, and beneath it was observed a thin silver-like layer so that the steel was not exposed. This may be a silver or silver-rich layer, but the reason for its being found on the steel is unknown. X-ray diffraction measurements detected a small amount of zinc-iron alloy in one of the specimens where the zinc was plated first. This was undesirable for reasons stated above.

The remaining alternative was to plate the silver on the steel first, so the problem of producing adherent silver deposits directly on S.A.E. 4130 steel was taken up once more. Success came easily. U. S. Patent 2,431,947 described an anodic treatment in phosphoric acid solution which purportedly caused a strong bond to be formed between the

TABLE 1. POTENTIAL-TIME DATA FOR ZINC-SILVER
DIFFUSION ALLOY (No. 4557-56A),
CONTAINING 25 PER CENT SILVER, IN
THREE PER CENT SODIUM CHLORIDE SOLUTION
AT 90°F., SATURATED-CALOMEL SCALE. VALUES
IN VOLTS.

Elapsed Time (Mins.)	Potential	Elapsed Time (Mins.)	Potential
1	-1.012	120	-0.911
10	-1.023	150	-0.914
20	-1.027	180	-0.922
30	-1.030	210	-0.919
40	-1.030	300	-0.912
50	-1.031	330	-0.913
60	-1.030		

steel and silver. A trial of the method showed the claims to be valid. The anodic treatment etched the steel uniformly, leaving a carbon smut on the surface, which was easily removed by brushing in a stream of tap water. The adherence of the silver was tested by heating the specimens at 500°F. for an hour. No separation of the silver from the steel occurred. Previously, electropolishing had been tried as a pretreatment, but the silver did not adhere. Apparently, a satisfactory mechanical bond is formed with the etched surface. Details of the anodic treatment are given in Appendix I.

A series of panels was prepared with a 0.0003-inch-thick zinc-silver diffusion alloy containing approximately 25% silver. Details of the electrodeposition are given in the experimental section and in Appendix I.

The X-ray results and the heat-treating data are given in Table 2. Characteristic photograms for each type of coating are shown in Figure 8*, Appendix II. Specimens 63A, 65A, and 72A showed the epsilon phase and silver to be present as given in photogram type 3, Figure 8. Free silver was estimated as being present to the extent of 2 to 3%. The necessary data for phase identification have been worked out by Owen and Pickup**. The epsilon phase has a hexagonal close-packed structure with a range in a_0 from 2.81 to 2.82 Å, and c_0 varies from 4.35 to 4.47 Å as the silver content varies from 20 to 46 weight per cent. The cell dimensions of the compound identified in these three specimens correspond to an alloy containing between 20 and 30% silver.

*The relative intensities in Figure 8 are estimated relative intensities for each photogram (with an exception), but can not be carried from one to another. The exception is the photogram for the zinc-silver epsilon phase. Here the relative intensities are represented as all being equal, because no intensity data were available.

**Proc. Roy. Soc., A, 140, 344 (1933).

TABLE 2. X-RAY DIFFRACTION STUDIES OF ZINC-SILVER
DIFFUSION ALLOY COATINGS, AND ZINC ON STEEL

Specimen Number	Per Cent Composition of Coating	Conditions for Diffusion	Order of Deposition	Phases Present by X-Ray Diffraction	Remarks
-65A	75 Zn - 25 Ag	500°F., 1 hr., N ₂ atmosphere	Zn first	Epsilon(1) phase + Ag(2)	See Figure 8, photograph Type 3.
-65A	Ditto	400°F., 2 hrs., oil	Zn first	Ditto	
-65A	"	Ditto	Ditto	Do + Zn + extra line at 2.27A	X-ray beam on thin place on sample.
-65A	Pure zinc	500°F., 1 hr., N ₂ atmosphere	-	Zinc	
-65A	Ditto	Ditto	-	Zinc + iron	Coating too thick. Part of it was etched off with dilute HCl.
-69B	Pure zinc	500°F., 1 hr., N ₂ atmosphere	-	Zinc	
-69B	Ditto	Ditto	-	Zinc + iron	Coating too thick. Part of it was etched off with dilute HCl.
-69C	Pure zinc	No diffusion	-	Zinc	This was run as a standard.
-72A	75 Zn - 25 Ag	500°F., 1 hr., N ₂ atmosphere	Ag first	Epsilon phase + Ag	
-73A	75 Zn - 25 Ag	250°F., 6 hrs., oil	Ag first	Epsilon phase + Ag + Zn	

(1) Phase nomenclature according to constitution diagram page 1155, ASM Metal Handbook, 1948 Edition.

(2) Estimated to be 2 to 3 per cent by weight.

Specimen 65A, which was heated in mineral oil at 400°F. for 2 hours, showed some free zinc at one location on the sample (see photogram type A, Figure 8, Appendix II). No explanation is known for the fact that 65A had free zinc in one place and not another. The presence of an extra line at 2.27Å might be attributed to the existence in this sample of a range of composition in epsilon phase. Specimen 73A, which was heated at 250°F. in oil for six hours, also had some free zinc (see photogram type A, Figure 8, Appendix II). These temperatures are probably too low. No experiments were conducted at higher temperatures in oil because the mineral oil had a flash point of 440°F.

During the time that these experiments were being carried on, a separate investigation was made to establish beyond doubt whether zinc and iron do interdiffuse at 500°F. Two S.A.E. 4130 steel panels were plated with 0.0003 inch of zinc. These were heated at 500°F. for one hour in a purified-nitrogen atmosphere. It was necessary to dissolve some of the coating off because the zinc pattern might have overshadowed the zinc-iron alloy lines, if any. No evidence of the interdiffusion of zinc and iron was found. Zinc was plated first in some of the subsequent tests, whereas silver was plated first in others.

In preparing specimens to be used for "wet-dry" exposure, diffusion was effected at 500°F. for one hour in a purified-nitrogen atmosphere.

The first signs of rust were observed on the zinc-silver coatings after four cycles in the "wet-dry" cabinet. The advance of rusting was very rapid. Two specimens which had been plated first with zinc were

heat treated in the same way and exposed in the "wet-dry" cabinet. These failed about as rapidly as the first group. These results are tabulated in Table 25, Appendix I.

The rapid deterioration of the diffusion-formed, zinc-silver-alloy coatings was unexpected, in view of the insignificant weight losses incurred by the cast specimens containing 25 per cent silver. (See Final Report, dated June 28, 1949.) What, if any, was the difference in the two alloys?

Two of the cast specimens from the early work were X-rayed. Pure epsilon phase (AgZn_3) was found with no trace of free silver. A small amount (3 to 5 per cent) of free silver was always found in the diffusion coatings that failed. Thus, with free silver, the potential relationships are favorable for rapid corrosion. The AgZn_3 has a potential about equal to that of zinc, while the potential for silver is more noble by over a volt. The results of the X-ray diffraction studies are given in Table 3, and typical photograms are given in Figure 9, Appendix II. When 3-1/2 hours of additional heat treatment was given to Specimen 4557-72A, the identification of the free silver was questionable, Specimen 4557-98A, which was heated for eight hours at the same 500°F. temperature, failed to show any free silver. (Standard AgZn_3 photogram, Figure 9.) The high-purity nitrogen that was used as an atmosphere during the heat treating contained small amounts of oxygen, which account for the presence of zinc oxide (Standard ZnO photogram, Figure 9, Appendix II).

In accomplishing the apparent solution of the silver, an undesirable condition was created. The coatings flaked from Specimens 4557-98A and 4557-98B, the latter being the more serious. A loose

TABLE 3. DESCRIPTION OF ZINC-SILVER DIFFUSION COATINGS AND
RESULTS OF X-RAY DIFFRACTION EXAMINATION

Specimen Number	Composition (Weight %)	Conditions For Diffusion	Order of Deposition	Remarks	Phases Identified by I-Ray Diffraction*
2375-62D1	24.9% Ag	---	---	Cast-alloy spectrometer record.	S-AgZn ₃ (epsilon)
-62D3	Ditto	---	---	Ditto	S-AgZn ₃
-62D1	"	---	---	Filings. Powder photograph.	S-AgZn ₃
4557-72A	23% Ag	1 Hr., 500°F.	Ag First	---	S-AgZn ₃ + VP-Ag
		3-1/2 Hrs., 500°F.	---	---	S-AgZn ₃ + Ag(?)
				Abraded lightly.	S-AgZn ₃ + Ag(?)
				More abrasion.	S-AgZn + P-Fe
4557-93A	28% Ag	8 Hrs., 500°F.	Zn First	Coating flaked.	S-AgZn ₃
				Loose flake from -93A.	S-AgZn ₃ + P-Zn
4557-98B	23.6% Ag	1 Hr., 500°F. +			
		1 Hr., 700°F. +			
		2 Hrs., 800°F.	Zn First	Coating flaked more than 4557-93A.	S-AgZn ₃ + P-Zn + P-ZnO
				Steel surface after removal of loose flake.	P-Fe + S-X**

* The letters S, MS, M, P, and VP refer to the relative intensities (strong, medium strong, medium, faint, and very faint) of that phase's diffraction pattern.

** X phase has not been positively identified, but it may be an Fe-Zn alloy.

flake from -98A had a small amount of free zinc. Free zinc probably would not be harmful, because the AgZn_3 has about the same potential as pure zinc.

Successive abrasions of Specimen 4557-98A showed that the AgZn_3 existed throughout the entire thickness of the coating. A private communication, received from the Standard Steel Spring Company, revealed that flaking was always associated with zinc deposited from a cyanide solution. They developed a special acid solution* which prevented flaking. It was also learned that, in the preparation of the zinc-nickel ("corronized") coatings, the nickel is deposited first and is covered with the zinc. Heat treating is done in air at 700°F., and diffusion is reported to be complete in thirty minutes. No visible oxidation takes place, but the resulting coating is a dark blue-gray in color.

Taking a cue from that work, an experiment was performed to see if the acid zinc solution would be effective in preventing flaking of zinc-silver coatings. Two sets of four specimens each were prepared with duplex zinc-silver coatings. These are the first eight specimens in Table 4. In all cases, the zinc was deposited first. Four specimens received zinc coatings from the cyanide solution, and the remaining four were coated in the special acid solution. All eight were silver plated in the same way. The two sets were heat treated simultaneously in air at 600°F. At the end of one, two, four, and eight hours, one specimen from each set was removed from the furnace. No flaking was observed in the "acid" specimens, but the "cyanide" specimens showed flaking. The acid specimens had a poor appearance, however.

*The composition of the special acid-type solution is not given in this report because no permission has been granted to do so.

TABLE 4. DESCRIPTION OF ZINC-SILVER DIFFUSION COATINGS AND RESULTS OF X-RAY DIFFRACTION EXAMINATION

Specimen Number	Composition (Weight %)	Order of Deposition	Type Bath For Zinc Deposition	Conditions For Diffusion	Remarks	Phases Identified by X-Ray Diffraction*
4557-98H	25.2% Ag	Zinc First	Cyanide	1 Hour, 600°F., Air	Blue-gray color. Coating peeled.	S-AgZn ₃ + VP-Ag
-98I	22.2% Ag	Ditto	Ditto	2 Hours, 600°F., Air	Ditto	S-AgZn ₃ + VP-Ag
-98J	22.1% Ag	"	"	4 Hours, 600°F., Air	"	S-AgZn ₃ + VP-Ag
-98K	23.9% Ag	"	"	8 Hours, 600°F., Air	"	S-AgZn ₃ + VP-Ag
5327-35B	24.5% Ag	"	Acid	1 Hour, 600°F., Air	Mottled color. No peeling.	S-AgZn ₃ + VP-Ag
-35C	23.5% Ag	"	"	2 Hours, 600°F., Air	Ditto	S-AgZn ₃ + VP-Ag
-35F	25.0% Ag	"	"	4 Hours, 600°F., Air	"	S-AgZn ₃ + P-Ag
-35G	25.0% Ag	"	"	8 Hours, 600°F., Air	"	S-AgZn ₃ + VP-Ag
5327-43B	24.0% Ag**	Silver First	"	1 Hour, 600°F., Air	Lustrous mat. No peeling.	S-AgZn ₃ + VP-Ag
-43C	24.0% Ag**	Ditto	"	2 Hours, 600°F., Air	Ditto	S-AgZn ₃ + VP-Ag
-43D	24.0% Ag**	"	"	4 Hours, 600°F., Air	"	S-AgZn ₃ + P-Ag
-43E	24.0% Ag**	"	"	8 Hours, 600°F., Air	"	S-AgZn ₃ + P-Ag

* The letters S, MS, M, F, VP, and WP refer to the relative intensities (strong, medium strong, medium, faint, very faint, and very, very faint) of that phase's diffraction pattern.

** Nominal.

Previous results had shown that, after eight hours of heat treating, no free silver could be detected by X-ray diffraction. Table 4 shows that free silver may be present in spite of the longer heat treatment. Also, the fact that no silver is detected by X-ray diffraction is no assurance that very small amounts are not present.

The experiment was repeated with the silver being deposited first, and only the acid zinc solution was used. The resultant coatings showed no flaking. They had lustrous, mat surfaces; in fact, they looked better after heat treating than before. These specimens were exposed in the "wet-dry" cabinet and failed after only one cycle. No difference due to heat-treating time was observed.

The methods for plating the duplex specimens are described in Appendix I.

Apparently, the preparation of resistant zinc-silver coatings by diffusion is not practicable or will involve a longer research before success is attained. It may be that, in order to achieve a satisfactory coating, codeposition studies will have to be resumed.

The influence of the heat-treating atmosphere on the zinc-silver coatings was tested by diffusing several duplex-coated specimens in hydrogen. When exposed in the "wet-dry" cabinet, these specimens rusted as rapidly as those heat treated in air (two cycles). Two specimens, coated with a zinc-silver duplex, undiffused plate, were also exposed. They showed rusting after two cycles, also.

Duplex plates, such as those with the zinc on the outside, would be expected to protect steel longer than for two cycles. The zinc made up more than 0.2 mil of the total coating thickness (0.3 mil). A simple zinc coating of 0.2-mil thickness on steel would prevent rusting for a longer period. The free silver is then probably the cause for the rapid rusting. Whereas the test with duplex plates does not prove the belief, it does support the idea.

The possibility of the coating being porous was eliminated by testing electrographically. No pores were detected.

Tests on Galvanic Couples Formed From Aluminum and Zinc-Silver Alloys

There is a possible danger in the use of alloy coatings which contain noble metals for protecting steel parts of aircraft. If the corrosion products from the alloy come in contact with aluminum or its alloys, the noble metal might deposit (by chemical displacement) on the aluminum. Thus, a couple would be formed in which the aluminum would be anodic, and as such would corrode rather rapidly. Alloys containing copper, such as brass, are "bad actors" in this respect.

The above discussion could also apply to zinc-silver alloys, the corrosion products of which might contain small amounts of silver. If a metallic deposit of silver formed on aluminum, the latter might corrode.

To determine the amount of corrosion brought about by such combinations, a group of couples was exposed in the "wet-dry" cabinet. Two zinc-silver alloys were used, one containing 17 per cent silver, the other 25 per cent silver. Two types of aluminum were used, bare 24ST

and 24ST Alclad. The aluminum specimens measured four inches by one inch, and the zinc-silver alloy pieces were about 3/4 inch square. The zinc-silver alloy specimens were clamped to the aluminum at one end by means of the Lucite washers which support the specimens in the cabinet.

After 150 cycles (75 days), the couples were removed and examined. The aluminum was lightly corroded all over. There was no evidence of localized corrosion at the interface between the aluminum and the zinc-silver alloy, nor elsewhere.

The conditions in the "wet-dry" cabinet might not have been favorable for obtaining galvanic corrosion. The mechanism would require some dissolution of the zinc-silver alloy, with subsequent precipitation of silver on aluminum, thus forming a silver-aluminum couple, in which the aluminum is anodic.

As mentioned above, copper and copper alloys will act in this way so as to produce copper-aluminum couples. As a test of galvanic action in the "wet-dry" cabinet, several couples composed of aluminum and copper and aluminum and brass are now being exposed. The test has not been completed, but the results will be communicated at a later date.

Even though the zinc-silver diffusion coatings had little protective value, dropping them from further study is not yet recommended. It is still believed that zinc-silver alloy coatings, if properly prepared, will be protective.

Experiments on the Codeposition of Zinc and Lead

Lead is soluble in zinc to the extent of about one per cent. Beyond this amount, there is complete immiscibility of the metals at room temperature. Tests made early in this program on cast specimens

disclosed that one per cent lead was insufficient for making a significant improvement in corrosion resistance. An increase is desired in the amount of lead in a zinc-lead alloy to be used as a protective coating.

Electrodeposited alloys other than zinc-lead alloys have been prepared which show evidence of greater solubility than would be predicted from the constitution diagram. Electrodeposition, then, is one possibility for making such alloys.

During the first year of work on this project, the codeposition of zinc and lead from cyanide baths, containing tartrate and fluoride, was studied. Wide variations in plate composition were observed even when the plating conditions were apparently identical. No X-ray data were taken, so it is not known what types structure were obtained.

Assuming, however, that no variation from the phase diagram can be expected, a quasi-alloy can be visualized comprising a fine dispersion of lead in zinc. This may also be prepared by electrodeposition..

Attempts to codeposit zinc and lead from fluoborate solutions or zincate-plumbite solutions were unsuccessful. In all cases, lead alone deposited. Examples of these solutions will be found in Appendix I.

This work continued with a study of baths in which the lead exists as a complex chloride. Zinc does not form chloride complexes. In that way, it was hoped to suppress the lead ion concentration, so as to bring the respective deposition potentials close together.

Several lead-complexing agents were tested. What was sought was a lead complex which would have a very low concentration of lead ions

in solution. This would shift the lead potential toward that of zinc if the zinc was not complexed. The static electrode potential of a complex LiCl-PbCl_2 mixture was measured and compared with the potential of a nitrate solution containing the same concentration of lead. The results are given in Table 5. Complexing caused the potential to shift only 200 millivolts in the negative direction. The potential of a one-molal zinc chloride solution would be about -1.0 volt, on the saturated-calomel scale. This leaves a difference of 400 millivolts between the zinc potential and the lead potential in the complex solution. Assuming the respective deposition potentials to be close to these values, considerable polarization would be required, in the case of the lead, in order to have codeposition.

Zinc chloride is even more soluble than lithium chloride. According to the law of mass action, where the chloride ion concentration is increased the lead ion concentration will be decreased.

A concentrated zinc chloride solution was made up and a relatively small amount of lead chloride was added to it. Several plating experiments were made using this complex zinc-lead solution. Table 23, Appendix I, gives the details of the experiments. The best deposits were crystalline and treed, with the adherence being poor. Analysis of the lead in the deposit showed 95 per cent to 97.5 per cent. Since much higher zinc percentages were desired, it was not thought worth while to determine zinc except by difference.

TABLE 5. SINGLE ELECTRODE POTENTIALS OF LEAD IN
NITRATE SOLUTION AND COMPLEX CHLORIDE
SOLUTION. SATURATED-CALOMEL SCALE.
VALUES IN VOLTS. 90°F.

Elapsed Time (Mins.)	Nitrate Solution*	Complex Lead Chloride Solution**
3	—	-0.610
10	—	-0.611
13	-0.411	—
21	-0.411	-0.614
35	-0.415	-0.614
58	-0.407	-0.614
110	-0.413	-0.612
193	-0.409	-0.610
360	-0.405	-0.608

* Lead nitrate solution contains 41.3 g./l. $Pb(NO_3)_2$ or 25.8 g./l. lead.

** Complex chloride solution consists of 35 g./l. $PbCl_2$ or 25.8 g./l. lead in a saturated $LiCl$ solution.

Experiments on the Electrodeposition of Zinc-Tin Alloys

The electrodeposition of zinc-tin alloys was investigated by the Tin Research Institute. Their formulation has been used successfully in England in several commercial units. Attempts to duplicate the results at Battelle did not at first meet with success. It was necessary to increase the zinc concentration in order to get the desired plate composition. A study of the problem revealed that high-purity stannate must be used. In England stannate is made from virgin tin. In the United States, sodium stannate is usually made from tin-plate scrap and other tin scrap. Consequently, it contains organic and other impurities.

A sample of British stannate was procured and with it the recommended bath produced the desired plate composition.

High-purity stannate can now be obtained in this country from the Metal and Thermit Corporation, Rahway, New Jersey.

Research also revealed that the bath should be held at operating temperature several days before use. Apparently some of the chemical changes are slow in taking place.

Full directions for operating this bath are given in Appendix I.

Manganese-Tin Alloy Coatings

Experiments on the Codeposition of Manganese and Tin

The investigation of this alloy grew out of a conference with Air Force representatives when the decision was reached to abandon the manganese-silver alloy in its favor. The manganese-tin constitution

diagram discloses that tin is soluble in manganese to the extent of 8% at room temperature. With higher percentages, intermetallic and possibly brittle compounds are formed. Compositions in the solid-solution range then became the goal for alloy plates.

Preliminary experiments for the electrodeposition of manganese-tin alloys were reported in the Final Report dated June 28, 1949. The investigation has been continued with studies of the pyrophosphate solution and the thiocyanate solution. Neither of these solutions has produced a deposit of the desired composition.

The pyrophosphate-type solution produced the better appearing deposits, so it was used for the quantitative trials. By increasing the current density from 43 to 144 amps./sq.ft., the manganese content rose from 6.3% to 36%. A further increase in current density to 216 amps./sq.ft. raised the manganese content to 43%. It appeared that further increases in current density would result in smaller and smaller increases in manganese content. Thus, a 92% manganese deposit or higher from these solutions appears unattainable.

Lowering the tin content of the solution by 60% had very little effect on the plate composition.

Attempts to improve the pyrophosphate solution resulted in better appearing deposits, but the tin contents were still high. Experiments with a straight sulfate-type solution resulted in deposits having a tin content below 1%. Addition of a tartrate to the sulfate solution raised the tin content to the range 35-70%. The lower tin content was obtained

at high current densities. By raising the $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ concentration from 40 g./l. to 200 g./l., the tin content of the deposits was finally lowered to about 12%.

With both tartrate and oxalate present, the $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ concentration could be lowered to 40 g./l. to produce deposits with a tin content in the range desired. When the oxalate was used in the absence of tartrate, poor deposits of uncertain composition resulted. Furthermore, the tin precipitated at a pH of 5 with only the oxalate present. When both tartrate and oxalate were present, no precipitation took place up to pH 8, at which point the bath seemed to function best. Current efficiencies are of the order of 15%.

Details of the experimental manganese-tin plating are given in Tables 21 and 22, Appendix I.

Static-Potential Tests

Table 6 gives the results of the static electrode potential tests on electrodeposited manganese-tin alloys in 3% sodium chloride solution. The data show two discrepancies in this series. The alloy containing 17% tin has a more noble potential than the 40% tin alloy. The "72%" tin alloy has a potential value which is less noble than the one containing "65%" tin. One apparent explanation is that the analyses were in error. The analyses were made on separate specimens plated under the same conditions, so it is also possible that lack of reproducibility in plating is the cause.

TABLE 6. POTENTIAL-TIME DATA FOR ELECTRODEPOSITED MANGANESE-TIN ALLOYS IN THREE PER CENT SODIUM CHLORIDE SOLUTION AT 90°F. SATURATED-CALOMEL SCALE. VALUES IN VOLTS.*

Specimen Number	γ _{Sp} *	Volts at Elapsed Time of:					
		1 Min.	30 Mins.	60 Mins.	90 Mins.	120 Mins.	330 Mins.
5022-29A	0.0	1.390	1.285	1.307	1.295	1.281	1.238
5022-33B	0.4	-	1.325	1.309	1.293	1.286	1.301
5022-48B	17	1.197	1.203	1.172	1.157	1.133	1.143
5022-54D	40	1.191	1.312	1.246	1.200	1.175	1.170
5022-40B	59	0.768	0.730	0.879	0.913	0.917	0.911
5022-41A	65	-	0.660	0.635	0.620	0.608	0.492
5022-40A	72	0.780	0.937	0.941	0.940	0.939	0.948

* All values are negative.

One of the discrepancies in potential relationships was reflected in the degree of corrosion observed visually on the specimens. The "17%" tin alloy showed no brown corrosion products, while the "40%" tin alloy did. The specimens containing 59%, 65%, and 72% tin showed no brown corrosion products. Therefore, it is known that there are manganese-tin alloys having greater corrosion resistance than has pure manganese at least in 3% sodium chloride solution, and which can be expected to give sacrificial protection to steel. What is not known is the exact composition for these alloys.

Experiments on the Preparation of Manganese-Tin Alloy Coatings by Diffusion

Subsequent experiments with the manganese-tin-plating bath showed the reproducibility to be poor. As with the zinc-silver work, time was an important factor, so rather than trace the cause of poor reproducibility, alloy coatings were prepared by diffusion.

In the work with electrodeposited alloys, those with a fairly high (about 40%) tin content showed prospects of having good corrosion resistance and of providing sacrificial protection.

The diffusion coatings which were prepared contained about 40% tin. Manganese was first plated on electropolished S.A.E. 4130 steel. Previous experience had demonstrated that electropolishing was necessary. Apparently, there was something on the surface of the steel which interfered with manganese deposition and which was removed by electropolishing. This may not be true for other lots of the same alloy. The tin was

plated directly on the manganese. The manganese-plated panel must be immersed in the tin-plating solution with the current on. Also, at the instant of immersion and for about five seconds thereafter, the current density must be above that normally used in tin plating. If those precautions were not taken, the tin did not completely cover the manganese, and where it did cover it blistered. Details of the manganese-tin duplex plating experiments are given in Appendix I.

No X-ray data were at first available for manganese-tin alloys. Nevertheless, determination of the extent of diffusion was possible. Standard patterns for pure tin and for pure alpha manganese are known. No evidence of free tin or free manganese could be found, so the conclusion was drawn that complete diffusion had taken place. Data for this test are contained in Table 7 and Figure 8.

Under the impression that interdiffusion of the manganese and tin was complete, several panels were exposed in the "wet-dry" cabinet.

The manganese-tin coatings showed better inherent resistance to attack than the pure manganese coatings. The characteristic brown corrosion products did not appear so rapidly on the alloy coating as on the pure manganese specimens. One specimen (4557-86C) had only 50 per cent of its surface covered with the manganese-type corrosion products after forty cycles in the "wet-dry" cabinet. The pure manganese coatings were covered with the brown oxides after only two cycles. The other three alloy coatings, while not so resistant as 4557-86C, did show improved surface resistance. As for providing sacrificial protection, however, the pure manganese was the better. After 134 cycles, the steel

TABLE 7. DESCRIPTION OF MANGANESE-TIN DIFFUSION COATINGS
AND RESULTS OF X-RAY DIFFRACTION EXAMINATION

Specimen Number	Composition (Weight %)	Conditions For Diffusion	Order of Deposition	Remarks	Phases Identified By X-Ray Diffraction*
4557-07B	60 Mn - 40 Sn	3 Hrs., 400°F.	Mn First	X-ray data for Mn-Sn alloys were not available at this time.	No free Mn, no free Sn
4557-07A	60 Mn - 40 Sn	3 Hrs., 400°F.	Mn First	One month after heat treatment. 0.1 mil abraded off. Additional 0.1 mil abraded off.	S-Sn + F-MnSn ₂ S-Sn S-Sn + VF-Mn S-Sn + S-Mn
5327-15A	50 Mn - 50 Sn	11 Hrs., 400°F.	Mn First	Abraded lightly. 7 days after heat treating un-abraded surface. Reheated, 5 hrs., 400°F. Powder removed, underlying surface examined.	S-MnSn ₂ + extra line F-MnSn ₂ + F-Mn VF-MnSn ₂ + S-Sn S-Sn S-Sn
5327-24B	50 Mn - 50 Sn	5 Hrs., 400°F.	Mn first, but 6 alternate layers alternate together.	5 days after heat treating. Reheated, 5 hrs., 400°F. Powder removed, underlying surface examined.	S-MnSn ₂ VF-MnSn ₂ + S-Sn VF-MnSn ₂ + MS-Sn F-MnSn ₂ + M-Sn

* The letters S, MS, L, F, and VF refer to the relative intensities (strong, medium strong, medium, faint, and very faint) of that phase's diffraction pattern.

underneath pure manganese coating had not rusted. This was not the case with the alloy coatings. Three of them showed iron rust, which covered 5 per cent, 15 per cent, and 50 per cent of the surface, respectively. (See Table 24. Appendix II.)

A better interpretation of these results can be made in the light of X-ray diffraction measurements, and so this discussion will be deferred until later in this report, where the X-ray results will be discussed. Following this, it was planned to prepare a series of manganese-tin alloys of different compositions. Calculations were made for alloys containing 10 per cent, 25 per cent, 50 per cent, 75 per cent, and 90 per cent tin. They were to be used for the measurement of potentials, which would define the composition limits within which sacrificial protection would be expected.

Shortly after this work was started, X-ray data were found which gave the identifying characteristics for manganese-tin compounds*. With the new information, a diffraction pattern was made from Specimen 4557-87A. (Table 7 gives the results for this and other manganese-tin specimens. Figure 10, Appendix II, shows the type of photograms obtained from the X-ray measurements.) The conditions for the preparation of Specimen 4557-87A were the same as for the panels exposed in the "wet-dry" cabinet. The diffraction pattern showed strong tin and faint $MnSn_2$ (Standard tin and Type A photograms, Figure 10). Some time following this diffraction measurement, the specimen was observed to have developed a gray powder

*Hans Nowotny and K. Schubert, Metallforschung, 1, 17 (1946).

on its surface. This powder had not been there originally. The diffraction pattern obtained from this powdery surface showed only tin to be present. Successive abrasions showed the free-manganese pattern to be increasing in intensity (standard alpha-manganese photogram, Figure 10). Apparently, diffusion had not been complete. Also, with forty weight per cent tin, one would expect a compound such as Mn_3Sn , rather than $MnSn_2$. At this point, the preparation of the composition series of manganese-tin coatings was deferred until further tests were made in determining the conditions for diffusion.

Heat treating at the same temperature for a longer period (see Specimen 5327-18A, Table 7) resulted in a stronger $MnSn_2$ pattern. X-raying after abrasion again demonstrated that the $MnSn_2$ was only on the surface. Seven days following heat treatment, the powder had reappeared. After additional heat treatment, only tin was found. Several days later, the powder appeared once more. The surface underlying the powder was X-rayed and only tin was found.

These experiments were repeated, using, instead of a duplex plate, a coating with a total of six alternating layers, three each of manganese and tin. The total thickness was the same as with the duplex plate (0.3 mil). This was Specimen 5327-24B. Essentially the same results were obtained as previously.

The data from all these experiments show that the $MnSn_2$ is concentrated in the outer layers. One explanation is that the manganese migrates along the surfaces of the tin pores and finds its way to the

surface. This phenomenon of surface migration has been observed with several other metal pairs. No reference to its occurrence in the case of manganese and tin has been found. The thin coatings of tin used in this work are undoubtedly porous.

The only thought on the formation of the powder is that MnSn_2 is unstable and decomposes. Although manganese was not found when the powdered surface was X-rayed, it may have been present. Manganese does not give so strong a diffraction pattern as tin and could have been overshadowed.

The "wet-dry" tests can now be examined in a slightly different light. The so-called "manganese-tin diffusion coatings", as prepared thus far, appear to be triplex coatings, with a thin outer layer of MnSn_2 , an intermediate layer of tin, and an inner layer of manganese. Decomposition of the MnSn_2 layer would leave a duplex coating of tin and manganese. There is sufficient difference in potential between these two metals to cause rapid deterioration of the manganese, hence the rusting observed in three of the four "manganese-tin" coatings.

A few experiments were conducted where a manganese-coated steel panel was immersed in a molten stannous chloride bath. The manganese displaces tin in the solution and molten tin forms on the surface. The heat should cause the tin to diffuse into the manganese. A second inert-salt bath would be necessary after the requisite amount of tin is deposited. Diffusion could continue without additional deposition of tin.

Experiments on the preparation of manganese-tin diffusion coatings by electrodepositing tin on manganese in a fused-salt bath were discontinued because this method has too many practical disadvantages. The manganese and the tin tend to segregate, and only small amounts of $MnSn_2$ were detected.

In the previous work on manganese-tin, the heat treating was done below the melting point of tin. Heating a duplex manganese-tin plate above the melting point of tin did not increase the alloying; in fact, less alloying seemed to take place.

Examination of two of the codeposited specimens which were prepared some time ago disclosed an unidentifiable phase. This phase did not correspond to any of the phases reported in the literature. Free tin was also found, but no free manganese was evident.

Manganese-Zinc Alloy Coatings

Experiments on Manganese-Zinc Codeposition

Attempts to codeposit manganese and zinc began with a manganous sulfate bath to which was added varying amounts of zinc sulfate. It was found that the addition of one gram of $ZnSO_4 \cdot 7H_2O$ per liter of solution resulted in a bright deposit. Analysis of this deposit showed it to contain 90-95 per cent manganese. X-ray diffraction revealed an amorphous structure.

A rapid corrosion test was made on the bright deposits by placing several drops of distilled water on the surface. Within less than an hour the characteristic brown manganese corrosion products were visible, so that the inherent corrosion resistance of this coating appeared to be no better than that of pure manganese.

When two or three grams of zinc sulfate were added to the bath, a black deposit was formed. Changes in the plating variables did not result in a satisfactory plate when the zinc sulfate was higher than one gram per liter. The deposits were not improved by addition agents such as thiosulfate, gum arabic, licorice, and boric acid.

Experiments with Manganese-Zinc Diffusion Coatings

For the most part, the procedure in the preparation of diffused binary-alloy coatings has been to deposit the higher melting metal first. The manganese-zinc system was first attacked in this way. The initial problem, of course, centered on obtaining adherent zinc deposits over the manganese.

Poor results were obtained with the special acid-type zinc solution used in the zinc-silver work. The zinc deposit was severely blistered. After several strike solutions failed to deposit adherent coatings, a dilute zinc cyanide strike solution was prepared and, by its use, better results were obtained.

Specimens with 0.3-mil-thick coatings containing 25 per cent, 50 per cent, and 75 per cent manganese were prepared and heat treated at 600°F. in air, for varying periods of time. Visual examination showed that, after four hours, the surface had darkened somewhat in color. In general, very little surface oxidation occurred during heat treating. When the manganese was plated last, the surface oxidized heavily.

Table 8 gives the heat-treating data and the phases found by X-ray diffraction. Reference to Figure 2 and Table 8 shows that

TABLE 8. RESULTS OF X-RAY DIFFRACTION EXAMINATION OF
MANGANESE-ZINC DIFFUSION COATINGS. MANGANESE
PLATED FIRST, EXCEPT AS NOTED.

Specimen Number	Composition ¹ (Weight %)	Diffusion Treatment	Phases Identified ²
5486-26A	50Mn - 50Zn	8 Hrs., 600°F., Air	S-epsilon + F-beta Mn + VF-MnO
-34G ³	Ditto	23 Hrs., 600°F., Air	S-epsilon + MF-beta Mn + VF-MnO
-26F	"	4 Hrs., 600°F., Air	S-epsilon + VF-beta Mn + VF-MnO
-34D	"	7-1/2Hrs., 600°F., Air	S-epsilon + F-beta Mn
-38A	75Mn - 25Zn	15 Hrs., 600°F., Air	S-epsilon + MF-beta Mn
-38N	25Mn - 75Zn	15 Hrs., 600°F., Air	S-epsilon + F-beta Mn + VF-MnO
-74C	75Mn - 25Zn	7 Hrs., 600°F., Air Cooled to 140°F. in Furnace in 16 Hours.	M-epsilon + F-beta Mn
-68F	50Mn - 50Zn	Ditto	S-epsilon + VF-beta Mn
-68D	50Mn - 50Zn	"	S-epsilon + VF-beta Mn
-72D	25Mn - 75Zn	"	S-alpha + ? Mn

1. Nominal.

2. The letters S, MS, M, F, and VF (strong, medium strong, medium, faint, and very faint) refer to the relative intensities of the phases' diffraction pattern. A question mark denotes that the identification of the phase was doubtful.

3. Zinc plated first.

diffusion took place essentially in accordance with the phase diagram. The most recent manganese-zinc phase diagram is reproduced in this report because it may not be readily available. The phases present (in the case of the 50-50 alloy) were those stable at about 572°F. (300°C.). The presence of these phases was thought to be due to air quenching when the specimens were removed from the 600°F. furnace. Another group of duplex manganese-zinc-coated specimens was heat treated in the same way but was furnace cooled at a slow rate. The data in Table 8 show that the slow cooling made no change in the results, except in the case of the 25 per cent manganese alloy.

Several specimens were prepared where the zinc was deposited first. These specimens oxidized heavily during the heat treating.

Table 17, Appendix I, gives some typical plating experiments in the preparation of manganese-zinc duplex coatings.

Static-Potential Measurements on Diffused Manganese-Zinc Coatings

Table 9 gives the results of static-potential measurements for three compositions of manganese-zinc coatings. The measurements were made in 3 per cent sodium chloride solution at 90°F.

These data show that sacrificial protection of steel can be obtained from these compositions. This is expected, since each of the elements is anodic to steel. The values at 360 minutes are in proportion to the manganese content. At the finish of the test, the beakers containing the sodium chloride solution were observed. A small amount of brown precipitate lay at the bottom of the beaker in which the

TABLE 9. STATIC-POTENTIAL MEASUREMENTS OF DIFFUSED MANGANESE-ZINC COATINGS IN 3% NaCl SOLUTION, AT 90°F. SATURATED-CALOMEL SCALE. VALUES IN VOLTS. POTENTIAL VALUES FOR MANGANESE, ZINC, AND IRON ARE INCLUDED FOR COMPARISON.

Specimen Number	Manganese (Weight %)	Potential at Elapsed Time of:				
		1 Min.	30 Min.	60 Min.	240 Min.	360 Min.
3180 - 37C	100	-1.390	-1.317	-1.316	-	-
5486 - 38B	75	-1.282	-1.038	-1.042	-1.075	-1.107
- 70A	50	-1.177	-1.053	-1.053	-1.040	-1.039
-38J	25	-1.035	-1.030	-1.031	-1.024	-1.016
2875 - 50B (Pure zinc)	0	-1.048	-1.056	-1.061	-	-
2875 - 33B (SAE 4130 steel)	-	-0.619	-0.709	-0.707	-	-

75 per cent manganese panel was tested. An equal amount of white precipitate was found in the beaker which contained the 25 per cent manganese panel. A much smaller amount of precipitate was observed in the beaker which contained the 50 per cent manganese panel. It appears that the 75 per cent manganese alloy corrodes very much like pure manganese, while the 25 per cent manganese alloy corrodes more like zinc. The 50-50 alloy had the better corrosion resistance in 3% sodium chloride solution.

Exposure tests with manganese-zinc, diffusion-alloy-coated specimens show this combination to have promise. The 50-50 coating has greater resistance than zinc, but it is not so good as cadmium in the "wet-dry" test. This coating gives sacrificial protection and has an apparent advantage over pure manganese or pure zinc in that the corrosion products are more adherent and compact. Scattered, light-gray specks were observed on the surfaces of some of the specimens. (See Table 26, Appendix II, for details.)

One of the difficulties with the visual examination of these manganese alloys is the uncertainty in determining the initial rust. The color of the corrosion products of the coating hides the presence of iron rust. A non-destructive test on the corrosion product is required. Examination under ultraviolet light has been tried, but without success. Because of this difficulty, the determination of the first rust in several cases was questionable. The presence of rust was ascertained after the specimens were removed from the cabinet.

The 75 per cent manganese alloy corroded very much like pure manganese, as did the coating where the zinc had been plated first.

A second group of manganese-zinc alloys were exposed in the "wet-dry" cabinet. This group included three compositions, 25 per cent, 50 per cent, and 75 per cent manganese. The results are detailed in Table 27, Appendix II.

With the exception of two panels with coatings containing 25 per cent manganese, all the panels have lasted longer than those coated with pure zinc. This indicates that for improved resistance the coatings should contain about 50 per cent manganese.

During this second test, two of the panels showed small rust spots after a few cycles, but the rusted areas disappeared as the test progressed. This phenomenon had not been observed before. A possible explanation is that the nonferrous corrosion products covered up the iron rust, and that finally the iron rust became sufficiently voluminous so that it could be seen.

Manganese-Copper Alloy Coatings

No work was done on manganese-copper alloy coatings. It was mutually agreed that such work should be deferred until the Navy outdoor exposure tests on such coatings were completed. The development and preparation of the coatings was carried out by Graham, Crowley, and Associates* for the Airborne Equipment Division of the Bureau of Aeronautics under Contract No. NOa(s)9930.

*407 South Dearborn Street, Chicago 5, Illinois.
475 York Road, Jenkintown, Pennsylvania.

Manganese-Nickel Alloy Coatings

Experiments on the Codeposition of Manganese and Nickel

Codeposits of manganese and nickel were obtained using a regular manganese bath with small additions of nickel sulfate. Quantitative analysis showed these deposits to contain only 13% manganese. The deposits were not coherent.

Pyrophosphate solutions containing both manganese and nickel did not give alloy deposits. Manganese, alone, was deposited from the pyrophosphate solution.

The compositions of the solutions used and the plating conditions are given in Appendix I.

Experiments on the Preparation of Manganese-Nickel Coatings by Diffusion

In preparing manganese-nickel duplex plates, the manganese was deposited on the steel from the manganous sulfate solution. Sound nickel deposits on manganese were not possible from a Watts-type solution. For the most part, the nickel deposited in a blistered form, and, where it was not blistered, the adherence was poor.

A nickel strike solution (originally developed for plating on nickel die castings) was not effective in producing good deposits, either. Thin nickel deposits have been obtained in this laboratory from a cyanide bath. This was tried on the manganese and, after some experimental work,

was found to be effective. Because the cyanide solution stops depositing nickel when a flash plate has been attained, it was necessary to follow it with a plate from a Watts-type solution. Some typical runs are given in Table 18, Appendix I. The tests recorded in this table are the culmination of many unsuccessful attempts to make a manganese-nickel duplex plate. The heat-treating data, together with the X-ray results, are given in Table 10. The 75-25 composition was chosen for these tests on the basis of previous tests with cast alloys. (See Final Report dated June 25, 1949.)

When heat treating at 600°F. for 8 hours resulted in no detectable diffusion, the same specimens were reheated at 1000°F. for periods ranging from 1-1/2 hours to 21 hours. Table 22 shows that, with increasing time in the furnace, the nickel and manganese lines became weaker, until, at 21 hours, their identifications were questionable. At the same time, iron became stronger, and a new phase, tentatively called the X-phase, became apparent. This X-phase has not been identified as yet. More work on these diffusion alloys will be necessary to clarify this matter.

Experiments with Zinc-Chromium Diffusion Coatings

No report has been found in the literature that gives X-ray data for zinc-chromium alloys. Diffusion may be detected by X-ray diffraction in the absence of such data, if the X-ray pattern shows no free zinc or free chromium, but does show some unknown phase. Of course, this train of thought can lead to an erroneous conclusion, as in the case of manganese-tin.

TABLE 10. RESULTS OF X-RAY DIFFRACTION EXAMINATION
OF MANGANESE-NICKEL DIFFUSION COATINGS.
MANGANESE PLATED FIRST.

Specimen Number	Composition ¹ (Weight %)	Heat Treatment	Phases Identified ²
5486-62C	75Mn - 25Ni	1 Hr., 600°F., Air	S-Ni + F-Mn
-62D	Ditto	2 Hrs., 600°F., Air	Ditto
-62E	"	4-1/2 Hrs., 600°F., Air	"
-62F	"	6-1/2 Hrs., 600°F., Air	"
-62G	"	8 Hrs., 600°F., Air	"
<u>Additional Heat Treatment</u>			
5486-62C	75Mn - 25Ni	1-1/2 Hrs., 1000°F., Air	S-Ni + S-Mn + M-Fe + VVF-X ³
-62D	Ditto	3 Hrs., 1000°F., Air	S-Ni + S-Mn + M-Fe + VF-X
-62E	"	4-1/2 Hrs., 1000°F., Air	S-Ni + S-Mn + M-Fe + F-X
-62F	"	6-1/2 Hrs., 1000°F., Air	M-Ni + ?-Mn + S-Fe + MS-X
-62G	"	21 Hrs., 1000°F., Air	?-Ni + ?-Mn + S-Fe + S-X

1. Nominal.
2. The letters S, MS, M, F, VF, and VVF refer to the relative intensities (strong, medium strong, medium, very faint, and very, very faint) of the phases' diffraction patterns. A question mark denotes that the identification of the phase is doubtful.
3. X- phase has not been identified, but does not appear to be a Mn - Ni alloy. Some of the diffraction lines of this phase correspond to some of those of MnO. However, not all of the lines can be accounted for by this compound.

During the first year of work on this project, three compositions of zinc-chromium alloys were prepared in cast form. They contained 0.48 per cent, 2.04 per cent, and 5.36 per cent chromium, respectively. X-ray patterns were made for each of these alloys. The patterns showed an unidentified phase (the Y phase) to be present in the 2.04% and 5.36% alloys, the latter having the larger amount. The chromium contents of these alloys are relatively low, but it was thought, at the time, that the patterns might serve as guides in the diffusion work.

Duplex plates were prepared in two ways, with the zinc first and with the chromium first. Standard chromium and zinc (cyanide) solutions were used where the zinc was plated first. A special zinc strike solution was used for plating on the chromium. The solutions and conditions are given in Appendix II.

The results of the diffusion treatment are given in Table II. Some diffusion took place, as shown by the small amounts of Y phase. Diffusion probably did not proceed far.

Experiments with Cadmium-Chromium Diffusion Alloys

No X-ray data were found in the literature for cadmium-chromium alloys.

The cadmium was plated first, and no difficulty was encountered in depositing the chromium over it.

It was thought that the cadmium and chromium would interdiffuse at a relatively low temperature, but such was not the case. The results are given in Table II.

TABLE 11. DESCRIPTION OF CAST AND DIFFUSED ZINC-CHROMIUM ALLOYS
AND DIFFUSED CADMIUM-CHROMIUM ALLOYS AND RESULTS OF
X-RAY DIFFRACTION EXAMINATION

Specimen Number	Composition (weight %)	Order of Deposition	Conditions for Diffusion	Remarks	Phases Identified by X-Ray Diffraction(a)
3190-63A-1	0.42% Cr(b)	---	---	Cast alloy.	S-Zn
-63B-1	2.04% Cr(b)	---	---	Ditto	S-Zn + F-Y(c)
-63C-1	5.36% Cr(b)	---	---	"	S-Zn + MF-Y
5351-16A	11% Cr	Zn First	2 Hours, 400°F. 3 Hours, 500°F. 2 Hours, 600°F. 4 Hours, 700°F. N ₂ atmosphere	Cr flaked off. X-ray data obtained from pieces.	S-Cr + VVF-Y
-12C	27% Cr	Cr First	22 Hours, 600°F., Air	Negligible discoloration of surface. Appears more lustrous.	S-Zn + F-Cr + VF-Y
5351-21A	Cd 32 - Cr 18	Cd First	5 Hours, 500°F. N ₂ atmosphere.	---	S-Cr

(a) The letters S, MS, M, F, VF, and VVF refer to the relative intensities (strong, medium strong, medium, faint, very faint, and very, very faint) of that phase's diffraction pattern.

(b) Specimens -63A-1, B-1, and C-1 were cast in the early phases of this project.

(c) Y phase has not been identified.

Experiments with Manganese-Cadmium Diffusion Coatings

No special strike was necessary for plating cadmium over manganese. Good cadmium deposits were obtained from a standard bright cyanide solution at current density of about 18 amperes per square foot. This is somewhat lower than the usual 30 amperes per square foot customarily used with this bath. The only diffusion tests were made on panels having a 50-50 coating. In all cases manganese was plated first. No diffusion was detected after heat treating at 500°F. for six hours. Table 19, Appendix I, shows the plating conditions for preparing the duplex plates. Table 12 gives the heat-treating data and the results of the examination by X-ray diffraction.

Preparation of Outdoor Panels

The coated panels for outdoor exposure have been almost completed. The details of their preparation are given here and will be given again several years hence when the results of the outdoor exposure are reported.

First of all, the preparation of each type of panel required some preliminary experiments to determine the current-density conditions for good plate distribution. After this, the plating was fairly routine, except in the case of the manganese-coated panels. A calibration curve for the measurement of manganese plate thickness with the Magne-Gage was not available. The calibration was made by first testing the thickness magnetically, and then, using exactly the same spot, measuring the true thickness of a micro section with a microscope.

TABLE 12. RESULTS OF X-RAY DIFFRACTION EXAMINATION
OF MANGANESE-CADMIUM DIFFUSION COATINGS.
MANGANESE PLATED FIRST.

Specimen Number	Composition ¹ (Weight %)	Heat Treatment	Phases Identified ²
5486 - 92 E	50 Mn - 50Cd	1 Hr. 500°F., Air	S - CD + VVF CdO
- 92 F	Ditto	2 Hrs. " "	S - Cd
- 92 J	"	6 Hrs. " "	S - Cd

1. Nominal

2. The letters S and VVF (strong and very, very faint) refer to the relative intensities of the phases' diffraction patterns.

To date, the zinc-tin, pure manganese, and manganese panels have been coated. As this is being written, the zinc and cadmium standards are in preparation.

The plating rack, described in Appendix I, worked very well in producing deposits of uniform thickness.

Miscellaneous Experiments

Exposure Tests in the "Wet-Dry" Cabinet

Manganese Coatings with Tin Overlay. Manganese coatings will provide cathodic protection to the underlying steel. However, the manganese will deteriorate rapidly. As a means of reducing this rapid corrosion, thin coatings of tin plate were applied over the manganese.

Two tin-coating thicknesses, 0.00003 inch and 0.00006 inch, were used. Neither was effective in reducing the corrosion in the "wet-dry" cabinet. After one cycle, the surface of the metal was covered with brown spots. Flash coatings of tin are inherently porous and break down very quickly. Once this happens, acceleration of corrosion can be expected because of the formation of tin-manganese couples.

Cadmium-Silver Alloy Plate. These deposits, containing 8% silver, were exposed in the scratched and unscratched conditions. Both types showed rust after a single cycle. It is important to note that the corrosion progressed fairly slowly after the first appearance of rust. At the end of 100 cycles, the pure cadmium was in better condition than

the alloy. The latter exhibited rust spots and scattered white corrosion products, whereas the cadmium had fewer rust spots and no white corrosion products. The cadmium-silver plate appears slightly inferior to the pure cadmium plate. While steel panels plated with zinc were not exposed concurrently, it is judged, on the basis of previous tests, that the cadmium-silver is superior to the pure zinc.

Weight-Loss Results on the Cadmium-Silver Castings. Reference to Table 13 shows that cadmium-silver has about the same resistance to corrosion in the "wet-dry" test as has pure cadmium.

Zinc-Nickel ("Corronized") Coatings. The results for the "corronized" coatings are given in Table 26, Appendix II.

Three coating compositions were exposed. In all cases, the "corronized" coatings rusted before the pure zinc coatings, which were exposed as standards. The progress of corrosion, following the initial rusting, varied with the composition. The higher the nickel, the slower the advance of rusting. It appears, from the results of this test, that, under conditions of moisture condensation, such as are met with in the tropics, these zinc-nickel alloys would not afford protection for steel. Observations of scratched zinc-nickel-coated specimens revealed that only a low degree of sacrificial protection could be expected where condensed moisture prevailed.

Whereas the nickel-zinc corronized coating appears to have achieved success under other atmospheric conditions, the results in the "wet-dry" test do not show such a coating to be a prospect for better protection than pure zinc in the tropics.

TABLE 10. WEIGHT LOSSES IN MILLIGRAMS PER SQUARE
DECIMETER PER DAY FOR CAST CADMIUM-
SILVER SPECIMENS AND CAST CADMIUM SPECI-
MENS AFTER 30 DAYS EXPOSURE TO THE
WET-DRY PROGRAM TEST.

% Ag	Specimen Number	Weight Loss (mdd)	Specimen Number	Weight Loss (mdd)	Average Weight Loss (mdd)
0.0	2875-50A	1.33	3180-19F	1.47	1.40
1.24	2875-60A1	1.30	2875-60A2	1.47	1.39
3.04	2875-60B1	1.22	2875-60B3	1.38	1.30
7.95	2875-60C1	1.41	2875-60C2	1.29	1.35

Cadmium-Tin Coatings. Both diffused and codeposited cadmium-tin alloy coatings were tested.

The specimens were supplied by the Naval Air Experimental Station, Naval Air Material Center, Navy Yard, Philadelphia, Pennsylvania. The diffused specimens measured 1-1/2 inches by 5 inches, and the coating ranged from 0.35 mil to 0.43 mil in thickness, as compared with the 0.3-mil coatings prepared here. The cadmium-tin coatings which were codeposited from a fluoborate solution were plated on 2-inch by 3-inch specimens and represented thicknesses from 0.05 mil to 0.3 mil. Taking these variations into consideration, the codeposited alloy is believed to be somewhat more resistant than the diffused coatings. Of the cadmium-tin coatings, only the codeposited 0.3-mil-thick (3393-66L) coating prevented rusting and did not show tarnishing. The only change was a slight darkening. (See Table 25, Appendix II, for details.)

A report* received from the Naval Air Experimental Station, Naval Air Material Center, Navy Yard, Philadelphia, discloses that the cadmium-tin-alloy coating deposited from a fluoborate solution is superior to both diffused cadmium-tin coatings and cadmium-plated coatings in the salt-spray and humidity tests. Atmospheric-exposure tests indicated that the fluoborate-alloy coating and pure cadmium were comparable in the protection afforded and both were superior to the diffusion-alloy coating.

*Report No. ALL NAM AE 411027, Part II, Tin-Cadmium Alloy Coatings - Report of Tests, Issued 12 May, 1950.

A recent publication* by B. E. Scott and R. D. Gray, Jr., of Wright-Aeronautical Corporation, gives salt-spray results for the cadmium-tin fluoborate coating. They report no rusting after 30 months in the salt-spray cabinet for coatings 0.4 and 0.5 mil in thickness.

Static-potential measurements in 3.5 sodium chloride solution were made on the specimens from the Navy. This was done to determine whether the coatings could give sacrificial protection to the steel. The values are given in Table 28, Appendix II.

Coatings Which Do Not Give Cathodic Protection. Recently, some thought has been given to the possibility of investigating coatings which do not give sacrificial protection to steel, but which are not much more noble than steel. The initial test of this idea was made using a codeposited iron-chromium alloy. The method for depositing this alloy has been developed at Battelle under the sponsorship of the Army Ordnance Department. This alloy contains 5 per cent iron and 95 per cent chromium, and is deposited from a tri-valent chromium bath. Unlike the chromium deposit from the usual chromic acid solution, this alloy plate is free of cracks. It was thought that the crack-free nature of the plate would provide greater protection of the underlying steel. Specimens coated with regular hard chromium were exposed simultaneously as controls.

Rust appeared on the iron-chromium and the chromium-coated panels after two cycles. Two of the iron-chromium specimens were removed after 24 cycles, and the remaining two, after 64 cycles. The

*Iron Age, January 18, pp. 59-62, 1951.

amount of rust was about the same on all four panels. The progress of rusting, beyond a certain point, is slow. Detailed results are given in Table 26, Appendix II.

Since experiments were being made with the electrodeposition of zinc-lead alloys, some pure lead coatings were exposed for comparison. After two cycles, the panels were covered with loose, white corrosion products. After four cycles, spots of rust showed.

The Effect of Lightly Nitrided Surfaces on the Corrosion of Zinc Plate. A short investigation was made on the effect of nitriding the steel surface prior to plating. Zinc plate was used for this study, because more information is available on the behavior of zinc plate than for any other coating in the "wet-dry" test.

~~The panels with nitrided surface~~ required an average of thirty cycles for initial rusting. The unnitrided panels showed the first rust after only 20 cycles. The advance of rust following the initial rusting was very rapid in both cases. The nonnitrided panels had 50% of the surface rusted after an average of 76 cycles, and the nitrided panels showed 50% rust after an average of 78 cycles. It can be concluded that, even though the nitriding delays the initial attack, the subsequent spread of rusting is so rapid that the difference in initial rusting has little or no meaning.

During World War II, it was reported that nitriding the surface of Armed Forces' tableware prior to chromium plating resulted in a higher degree of corrosion resistance than offered by chromium-plated

unnitrided steel. The type of plate which is deposited over the nitrided surface may also influence the results.

A Proposed Graphical Method for Improving the Interpretation of "Wet-Dry" Tests. If the number of cycles to initial rust are used as a sole criterion of corrosion resistance, it is entirely possible to draw false conclusions. Such would be the case with manganese-zinc plate on which one or two spots of rust appear after only two cycles. Assume that the initial rusting on a zinc-coated-panel occurs after twenty cycles. The zinc-coated panel may be 50 per cent corroded at seventy cycles, whereas the manganese-zinc-coated steel, which rusted first, is only five per cent corroded at seventy cycles. Thus, the progress of further rusting after the initial rust is also an important factor.

It is proposed, therefore, to introduce a graphical integration method which includes the initial rusting and the progress of rusting thereafter.

Figure 3 illustrates this method. The limit for recording the extent of surface rusting has been arbitrarily chosen as 50 per cent. A lower percentage can be taken if desired. The ordinate is chosen as the per cent area rusted, while the number of cycles are recorded along the abscissa. By taking the area of the shaded sections in Figure 3, a number is obtained (the "index") which gives the relative resistance of a coating. The upper curve shows how a zinc-coated panel might be represented. The lower drawing in Figure 3, which might symbolize the corrosion factor for manganese-zinc, shows earlier rusting but a very

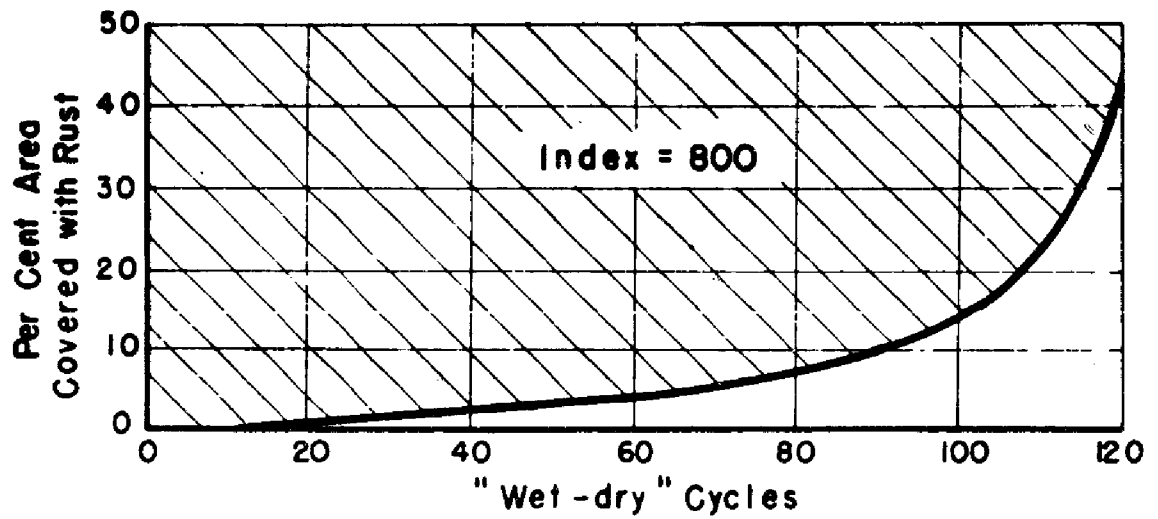
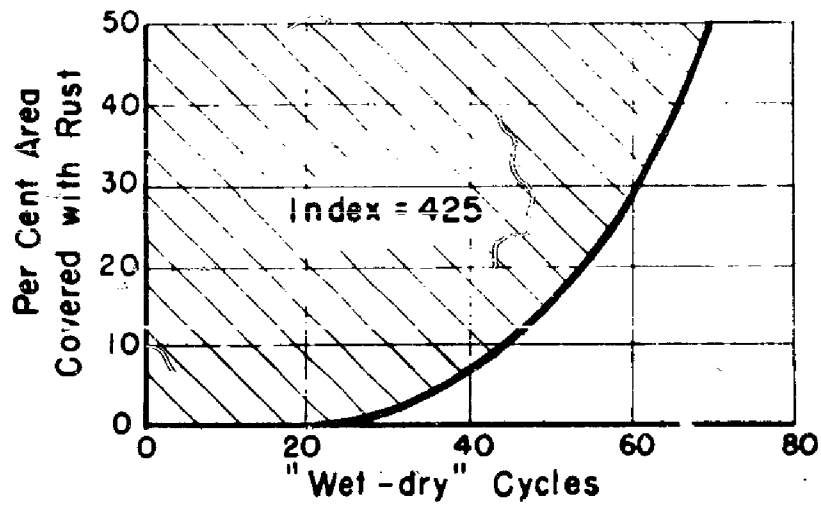


FIGURE 3. EXAMPLES OF A GRAPHICAL METHOD FOR INTERPRETATION OF "WET-DRY" TESTS

slow advance of rust. The indexes show that the overall protective value of manganese-zinc is greater than that of zinc alone.

The method does not allow for differences in depth of penetration of the corrosion. During the three years that the "wet-dry" test has been in use, large differences have not been observed. If it is found in the future that there are significant variations in depth of penetration, then this factor can be added in.

The graphical method has been applied to some of the more recent tests. Table 27, Appendix II, gives the index values for plain zinc plate, zinc plate on a nitrided steel surface, and various compositions of manganese-zinc coating. The average index value for plain zinc is 439 and that for zinc on nitrided steel is 462. The index for the nitrided specimens is slightly larger, but not large enough to mean that an improvement has been brought about by nitriding the steel surface.

The results for manganese-zinc coatings show much larger deviations than do the aforementioned tests. Because of this, it may be necessary to apply statistical treatment to the results. This possibility is being studied. For the present, averages will be used. For the 25% manganese coating, the average index is 684, for the 50% manganese coating it is 878, and for the 75% manganese coating the value is 1187. <

The main purpose in applying the graphical method to these tests at this time is to illustrate its use. It is believed that with refinements it can be developed into a useful tool.

Investigation of Corrosion Products. For some time it has been planned to study the corrosion products of the various coatings. One objective is to determine the influence of the alloying elements on the nature and extent of corrosion products. Knowing this, "designing" an alloy coating for maximum protection would be possible.

Preliminary studies of manganese-zinc corrosion products are given in Table 14. It is seen that zinc does influence the nature of the corrosion products. No attempt is made at the present time to correlate this information with other corrosion data. Further studies should be made before this is done.

EXPERIMENTAL WORK*

The apparatus and methods used for this work are described in detail in Appendix I. Appendix II is a collection of tabulated experimental data.

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- *Laboratory Record Book No. 3393, pp. 57-100.
 - Laboratory Record Book No. 4557, pp. 4-100.
 - Laboratory Record Book No. 5022, pp. 1-67.
 - Laboratory Record Book No. 5327, pp. 1-58.
 - Laboratory Record Book No. 5351, pp. 1-81.
 - Laboratory Record Book No. 5486, pp. 1-100.
 - Laboratory Record Book No. 5561, pp. 1-30.
 - Laboratory Record Book No. 5617, pp. 1-23.

TABLE 14. X-RAY DIFFRACTION RESULTS ON MANGANESE-ZINC CORROSION PRODUCTS

Specimen Number	Plate Composition (Feight %)	$Mn_2O_3 \cdot H_2O$	Mn_3O_4	Unidentified Phase
4557-89B	100%Mn	Strong	--	--
5486-38F	75Mn - 25Zn	Medium	Strong	Very Faint
-76H	50Mn - 50Zn	--	Ditto	Medium
-76D	25Mn - 75Zn	--	"	Medium

FUTURE WORK

The future work comprises two phases under an extension of the contract:

1. Outdoor exposure of the coatings discussed earlier in this report.

2. Investigation of methods for electrodepositing binary manganese alloys. The manganese-zinc, manganese-tin, manganese-copper, manganese-iron, manganese-molybdenum, manganese-nickel, and manganese-chromium systems will be studied, with the emphasis on the first two systems.

APPENDIX I

This Appendix contains descriptions of apparatus and methods used for the work described herein.

Preparation of Three Per Cent Sodium Chloride Solution for Static-Potential Measurements

The water used for the sodium chloride solution was the regular laboratory distilled water having a pH of 6.3. The salt was "Baker's Analysed" chemically pure sodium chloride. The solution was filtered and the concentration checked by accurate specific gravity measurement.

Static Electrode Potential Measurements

Apparatus

Figure 4 is a picture of the apparatus as set up for measuring static electrode potentials of four specimens concurrently. Also, pictured in the figure are the additional pieces of equipment used in the dynamic-potential measurements. No dynamic potentials were measured during the current phase of this project because of reasons given earlier in this report.

A Leeds and Northrup student-type potentiometer was used for making the static-potential measurements. Beckman No. 4970 saturated-calomel electrodes* were used as reference electrodes. Originally, a

*Manufactured by the National Technical Labs., Pasadena, California.



Figure 4. Apparatus for the Measurement of Static and Dynamic Electrode Potentials and Corrosion Currents. As Pictured, the Apparatus is Connected to Measure Static Electrode Potentials.

capillary bridge was used with the Beckman electrodes. The capillary bridge was replaced early in this work with a salt-bridge junction tube described by G. A. Perley*. This bridge is nothing more than a Pyrex test tube with a soft glass rivet blown into a hole in the lower end. On cooling, the soft glass rivet contracts slightly more than the Pyrex, leaving a fine capillary crack. This crack is fine enough to keep the solutions on each side of the rivet from interdiffusing, but large enough to allow electrolytic conductivity. It has an advantage, too, in that it is more quickly set up than the former type.

The salt solutions were contained in 250-ml. beakers, which were immersed in a thermostatically controlled water bath (WB in Figure 4), which operated within $\pm 1^\circ\text{F}$. of the desired temperature.

The specimens were supported in bakelite clamps which rested on the edges of the beakers. A four-way, rotating, double-pole switch (S_3 in Figure 4) was used so as to make possible the concurrent measurement of four cells.

The potentiometric circuit was calibrated twice by the Battelle Instrument Laboratory and was found to be accurate to 0.5 millivolt.

Method

Five milliliters of saturated potassium chloride solution were placed in the Perley-type bridge, the lower end of which was then immersed in the sodium chloride solution. The Beckman calomel electrode

*Trans. Electrochem. Soc., 92, 497 (1947).

was next immersed in the potassium chloride solution in the Porley bridge. The bridge was then adjusted so that the level of the sodium chloride solution is above that of the potassium chloride solution. In this way, any diffusion of the potassium chloride into the sodium chloride is minimized.

The clamped specimen was then immersed in the sodium chloride solution. After one minute, the initial potential measurement was made. This short elapse of time allows the specimen to "settle down" to a point where the potential is not changing very rapidly. Subsequent measurements were made at whatever time intervals desired.

The "Wet-Dry Program" Cabinet

A lead-lined, cork-insulated plywood box, measuring 34 inches x 25 inches x 25 inches, is the basis for the "wet-dry program" cabinet pictured in Figure 5. This box is equipped with a 1/2-inch-thick Lucite door (A) (letters in parenthesis refer to Figure 5), on which the specimens are supported by being clamped between Lucite washers in such a way that the test pieces do not make contact with the 18-8 stainless steel machine screws which pass through the washers. Twenty-four specimens can be exposed simultaneously. To prevent warping of the Lucite door, the edges were bound with angle iron.

The Lucite door is opened and closed in a predetermined cycle by a small motor (B), which, in turn, is actuated by a timing device (C) operating through relay (D). The motor (B) is a special type having two field coils, one of which "shades" the other, causing reversal.



Figure 5. "Wet-Dry Program" Cabinet. Showing Door Open and Corroding Specimens in Place.

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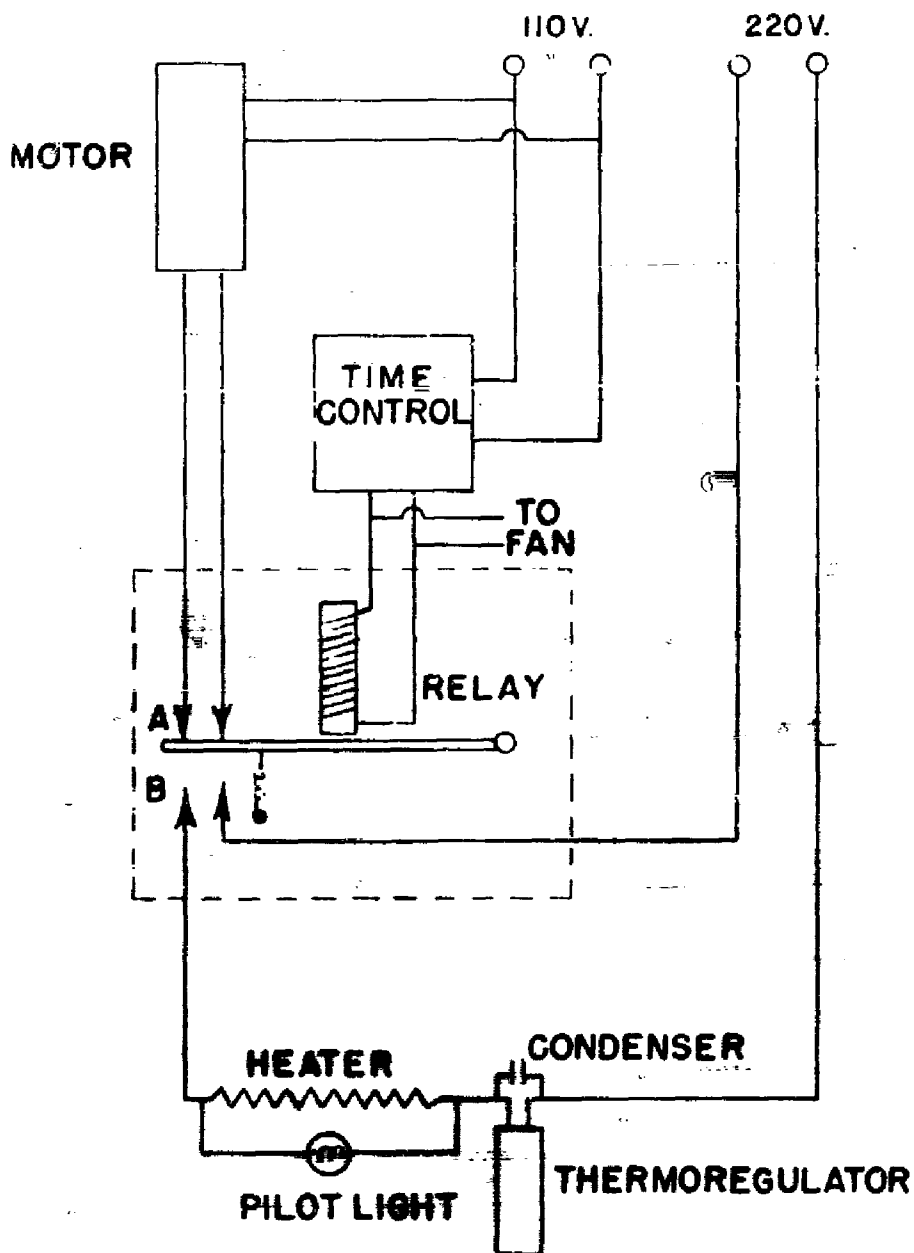


FIGURE 6. SCHEMATIC DIAGRAM OF ELECTRICAL CIRCUIT FOR "WET-DRY PROGRAM" CABINET.

tabs on the circular time-setting plate could not be set for an interval as small as one hour.

Heater - Lo-Lag, 2000-watt, 230-volt copper-clad immersion heater.

American Instrument Co., Silver Spring, Maryland.

Relay - Double-pole, double-throw relay. Struthers-Dunn, Inc.,

Philadelphia, Pennsylvania. (Note: In Figure 6, the

relay was not represented as being of the DPDT type for reasons of simplicity.).

Thermoregulator - Two, 110-volt, 10-amp. thermostats connected

in series. Fenwall, Inc., Ashland, Massachusetts.

Removal of Corrosion Products for Weight-Loss Tests

The corrosion products were removed from the cadmium-silver castings and the pure cadmium castings by immersing the test pieces in 100 ml. of a 1 per cent solution of sodium cyanide at 70°F. for 20 minutes. After 10 minutes had elapsed, the surfaces were brushed lightly while the specimen was still immersed. A second 20-minute immersion in a fresh portion of solution, with brushing as above, completed the removal of the corrosion products. Blank tests showed the above treatment to remove only insignificant amounts of metal. Each specimen was examined at 20X magnification with a binocular microscope to be sure all nonmetallic material had been removed. The specimens were then reweighed and the weight-loss calculations made.

Preparation of Experimental Diffusion Coatings

Apparatus

The plating apparatus used in preparing the duplex deposits preparatory to diffusion was in no way unusual. One- to three-liter quantities of plating solutions were used, and these were contained in Pyrex beakers. Heat was supplied to the solutions by thermostatically controlled glass-sheathed immersion heaters or by thermostatically controlled hot plates. The direct-current source was a 15-volt generator. The current was controlled by variable resistors, and Weston laboratory-model voltmeters and ammeters were used for voltage and current readings.

After the duplex plates had been prepared, they were heat treated in one of three ways to cause interdiffusion and alloy formation. At first, when it was believed that an inert atmosphere was required, the heat treating was done in a tube furnace. Later, the heat treating was done in regular heat-treating furnaces with an air atmosphere. A few specimens were diffused at 400°F. in a mineral oil bath. This temperature was too low, and was not raised because the oil had a flash point of 440°F.

Methods

Preliminary duplex plates were made on 1-inch x 4-inches x .015-inch SAE 1010 steel panels. Occasionally some of these were used in subsequent testing, but for the most part SAE 4130 panels measuring 1 inch x 4 inches x 0.063 inch were used for "wet-dry" and other testing.

The SAE 4130 test pieces were cut from strips measuring 4 inches x 18 inches, which had first been belt polished to a 240-grit finish. The 1 x 4-inch test pieces were then numbered and stored in oil until used.

The plating methods are discussed individually below.

Zinc-Silver. The plating solutions, conditions, and finishing sequences for the zinc-silver duplex plating are given in this section.

Table 15 contains weight of coating data for several typical samples.

Anodic Phosphate Treatment for Promoting
Adhesion of Silver to Steel

H ₃ PO ₄ (85%)	500 ml.
H ₂ O	500 ml.
Temperature:	130°F.
Current Density:	100 ASF
Time:	2 minutes
Cathodes:	Stainless steel

First Silver Strike

AgCN	2.0 g./l.
KCN (free)	150 g./l.
Temperature: —	80°F.
Current Density:	5 ASF

TABLE 15. RESPECTIVE WEIGHTS OF SILVER AND ZINC IN
 DUPLEX COATINGS WHICH WERE DIFFUSED AT
 500°F. FOR ONE HOUR AND EXPOSED IN WET-
 DRY CABINET. SURFACE AREA: SIX SQUARE
 INCHES.

	4557-75A	4557-75B	4557-75C	4557-75D
Weight of silver, g.	0.0729	0.0771	0.0742	0.0741
Weight of zinc, g.	0.2516	0.2519	0.2523	0.2521
Per cent silver	22.5	23.4	22.7	22.7

Zinc Plate*

Zn(CN) ₂	90 g./l.
NaCN	37.5 g./l.
NaOH	90 g./l.
Temperature:	120°F.
Current Density:	60 ASF
Anodes:	Zinc

Cyanide Dip

KCN	100 g./l.
-----	-----------

Alkaline Cleaner (Anodic)

Anodex**	75 g/l.
Temperature:	200°F.
Current Density:	100 ASF

Finishing Sequence for Zinc-Silver Duplex Plating

- (1) Anodic, alkaline clean, 1 minute.
- (2) Hot-water rinse.
- (3) Anodic, phosphate treatment, 2 minutes.
- (4) Hot-water rinse.
- (5) Cyanide dip, 10-20 seconds.

*This bath was used at first but was later replaced by a special acid solution developed for another sponsor. No permission has been granted to reveal its composition.

**MacDermid, Inc., Waterbury 20, Conn.

- (6) First silver strike, 20 seconds.
- (7) Silver plate, 5 minutes.
- (8) Distilled-water rinse.
- (9) Cyanide dip.
- (10) Zinc plate, 5 minutes.
- (11) Cold-water rinse and dry.

Manganese-Tin. The plating solutions, conditions, and finishing sequences for the manganese-tin duplex plating are given in this section. Table 16 gives some typical examples of manganese-tin duplex plating.

Manganese-Plating Solution

$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	40 g./l.
$(\text{NH}_4)_2\text{SO}_4$	135 g./l.
$\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$	0.5 g./l.
Temperature:	100°F.
Current Density:	45 ASF
Anodes:	Carbon rods in Alundum cups
Anolyte: $(\text{NH}_4)_2\text{SO}_4$	135 g./l.
pH:	7.5

Tin-Plating Solution

$\text{K}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$	100 g./l.
NaOH	7.5 g./l.

TABLE 16. PREPARATION OF MANGANESE-TIN DUPLEX COATINGS

Specimen Number	Temp., °F.	Manganese Plating				Tin Plating				Time (Min.)	Remarks		
		Amps.	C.D. (ASF)	Volts	Temp., °F.	Amps.		C.D. (ASF)					
						Initial	Final	Initial	Final				
"Tummy"	102	1.9	45	4	7.5	178	1.25	0.85	30	20	2.5	7	Manganese deposit blistered at high-current-density edges.
4457 - 86A	102	1.9	45	-	7.5	-	-	-	-	-	-	-	Tin blistered. Added 10 ml. sulfite solution (0.1 g. $\text{Na}_2\text{S}_3\text{O}_5 \cdot 7\text{H}_2\text{O}/\text{ml.}$) to manganese bath.
- 86B	102	1.9	45	-	7.5	161	1.25	0.85	30	20	-	7	Tin blistered during plating. Manganese bath pH 7.6. Add 4 ml. sulfite solution.
"Tummy"	102	1.9	45	-	7.5	-	0.85	0.85	20	20	-	-	Tin blistered.
"Tummy"	96	1.9	45	-	7.5	175	0.85	0.85	20	20	-	7	Excellent adherent deposit.
4457 - 86C	100	1.9	45	-	7.5	173	3.0	0.80	72	19	-	7	Ditto
- 86D	100	1.9	45	-	7.5	174	2.5	0.80	60	19	-	7	This specimen analysed 42.94 tin.
- 86E	100	1.9	45	-	7.5	174	2.7	0.80	65	19	-	7	Excellent adherent deposit.
- 86F	100	1.9	45	3.8	7.5	175	2.0	0.80	48	19	2.5	7	Ditto
- 86G	101	1.9	45	-	7.5	174	2.9	0.80	70	19	-	7	Ditto
- 86H	101	1.7	45	-	7.5	174	2.1	0.80	50	19	-	7	This specimen analysed 40.27 tin. Added 10 ml. sulfite solution to manganese bath.
- 87A	102	1.9	45	3.8	7.5	174	2.8	0.80	67	19	2.5	7	Excellent adherent deposit.
- 87B	102	1.9	45	-	7.5	174	3.0	0.80	72	19	-	7	Ditto
- 87C	102	1.9	45	-	7.5	175	1.7	0.80	41	19	-	7	This specimen analysed 41.28 tin.

* The current was maintained at this value for five seconds. The manganese-coated panel entered the tin solution with the current on.

Temperature: 175°F.
Current Density: 20 ASF
Anodes: Steel

Finishing Sequence for Manganese-Tin
Duplex Plates

- (1) Electropolish*, 5 minutes.
- (2) Alkaline clean, anodic, 1 minute.
- (3) Hot-water rinse.
- (4) HCl dip (1 vol. 37% HCl, 3 vols. H₂O), 3 seconds, 70°F.
- (5) Cold-water rinse.
- (6) Manganese plate, 7-1/2 minutes.
- (7) Distilled-water rinse.
- (8) Tin plate. Enter solution with current on. (See Table
16 for time and current values.)
- (9) Rinse and dry.

Manganese-Zinc. The plating solutions, conditions, and finishing sequences for the manganese-zinc duplex plating are given in this section. Table 17 gives some typical examples of manganese-zinc duplex plating.

Manganese-Plating Solution

MnSO ₄ ·H ₂ O	40 g./l.
(NH ₄) ₂ SO ₄	135 g./l.
Na ₂ SO ₃ ·7H ₂ O	0.5 g./l.

* Process of Battelle Development Corporation, Columbus 1, Ohio.

TABLE 17. SOME EXAMPLES OF THE PREPARATION OF
MANGANESE-ZINC DUPLEX COATINGS*

Specimen Number	Manganese Plating			Zinc Strike			Zinc Plate		
	Temp. (°F.)	Amps. (ASF)	C.D. Time (Min.)	Temp. (°F.)	Amps. (ASF)	C.D. Time (Sec.)	Temp. (°F.)	Amps. (ASF)	C.D. Time (Min.)
5486 - 26A	96	1.9	45	80	2.0	48	100	1.04	25
- 26F	100	1.9	"	80	1.70	41	100	1.04	"
- 34D	100	1.9	"	80	1.70	41	100	1.04	"
- 34G	100	1.9	"	80	- No strike -		100	1.04 (Zinc plated first)	5.08
- 38A	100	1.9	"	80	1.75	42	100	1.04	25
- 38H	100	1.9	"	80	1.70	41	100	1.04	"
- 68D	102	1.9	"	82	1.7	"	99	1.04	"
- 68F	-	1.9	"	82	1.7	"	98	1.04	"
- 72D	100	1.9	"	80	1.7	"	100	1.04	"
- 74C	102	1.9	"	80	1.7	"	100	1.04	"

* Except as noted, the plating took place as given above from left to right.

Temperature: 100°F.
Current Density: 45 ASF
Anodes: Carbon rods in Alundum cups
Anolyte: $(\text{NH}_4)_2\text{SO}_4$ 135 g./l.
pH: 7.5

Zinc Strike

Zn $(\text{CN})_2$ 5-7.5 g./l.
NaCN 5 g./l.
NaOH 5 g./l.

Temperature: 80°F.
Current Density: 40 ASF
Anodes: Stainless steel
Time: 1 minute
Note: Immerse manganese-plated panel
with current on.

Zinc-Plating Solution

Zn $(\text{CN})_2$ 90 g./l.
NaCN 37.5 g./l.
NaOH 90 g./l.
Temperature: 120°F.
Current Density: 50 ASF
Anodes: Pure zinc (bagged)

Finishing Sequence for Manganese-Zinc Duplex Plates

- (1) Electropolish*, 5 minutes.
 - (2) Alkaline clean, cathodic one minute, anodic 15 seconds.
 - (3) Hot-water rinse.
 - (4) H_2SO_4 dip (10% H_2SO_4), 10-15 secs., 80°F.
 - (5) Hot-water rinse.
 - (6) Manganese plate.
 - (7) Hot-water plus distilled water rinse.
 - (8) Zinc strike.
 - (9) Hot-water rinse plus distilled water rinse.
 - (10) Zinc plate.
 - (11) Rinse and dry.
-

Manganese-Nickel. The plating solutions, conditions, and finishing sequences for the manganese-nickel duplex plating are given in this section.

Table 18 contains plating data for some typical examples.

Manganese-Plating Solution

$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	40 g./l.
$(\text{NH}_4)_2\text{SO}_4$	135 g./l.
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$	0.5 g./l.

*Process of Battelle Development Corporation, Columbus 1, Ohio.

TABLE 18. SOME EXAMPLES OF THE PREPARATION OF
MANGANESE-NICKEL DUPLEX COATINGS*

Specimen Number	Manganese Plating			Nickel Strike			Nickel Plate					
	Temp. (°F.)	C.D. (ASF)	Time (Min.)	Temp. (°F.)	Amps. (ASF)	C.D. (Min.)	Temp. (°F.)	Amps. (ASF)	C.I. Time (Min.)			
5486 - 62C	98	1.9	45	8.17	80	1.0	24	15	135	1.67	40	2.0
- 62D	97	1.9	45	8.17	80	1.0	24	15	136	1.67	40	2.0
- 62E	97	1.9	45	8.17	80	1.0	24	15	138	1.67	40	2.0
- 62F	97	1.9	45	8.17	80	1.0	24	15	138	1.67	40	2.0
- 62G	97	1.9	45	8.17	80	1.0	24	15	136	1.67	40	2.0

* Plating took place as given above from left to right.

Temperature: 100°F.
Current Density: 45 ASF
Anodes: Carbon rods in Alundum cups
Anolyte: $(\text{NH}_4)_2\text{SO}_4$ 135 g./l.
pH: 7.5

Nickel Strike Solution for Plating on Manganese

$\text{Ni}(\text{CN})_2$ 91.3 g./l.
KCN 100 g./l.
 $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ 20 g./l.

Temperature: 80°F.
Current Density: 24 ASF
Anodes: Steel

Nickel-Plating Solution

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 300 g./l.
 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 50 g./l.
 H_3BO_3 35 g./l.
Harshaw XXX-D* 20 ml./l.

Note: This solution was purified by the usual methods.

* Harshaw Chemical Company, Cleveland, Ohio.

Temperature: 135°F.
Current Density: 40 ASF
Anodes: Cast nickel in bags
pH: 2.8

Finishing Sequence for Manganese-Nickel Duplex Plates

- (1) through (7) Same as for manganese-zinc.
- (8) Nickel strike.
- (9) Hot-water rinse plus distilled water rinse.
- (10) Nickel plate.
- (11) Rinse and dry.

Zinc-Chromium. The plating solutions, conditions, and finishing sequences for the zinc-chromium duplex plating are given in this section.

Chromium-Plating Solution

CrO ₃	250 g./l.
SO ₄	2.5 g./l.
Temperature:	120°F.
Current Density:	225 ASF
Anodes:	Antimonial lead

Zinc Strike

ZnO	2 g./l.
H ₂ SO ₄ (96%)	10 ml./l.
Temperature:	70°F.
Current Density:	120 ASF
Time:	15 seconds
Anodes:	Lead

Zinc-Plating Solution

Zn(CN) ₂	90 g./l.
NaCN	37.5 g./l.
NaOH	90 g./l.

Temperature:	120°F.
Current Density:	60 ASF
Anodes:	Zinc (bagged)

Finishing Sequence for Zinc-Chromium Duplex Plating when Zinc was Plated First

- (1) Alkaline clean, anodic, 1 minute, 50 ASF.
- (2) Hot-water rinse.
- (3) Acid dip, 3N H₂SO₄, 30 seconds, 80°F.
- (4) Cold-water rinse.
- (5) 10 seconds' dip in 10% NaCN solution, 70°F.
- (6) Cold-water rinse.

- (7) Zinc plate.
- (8) Hot-water rinse.
- (9) Chromium plate.

Finishing Sequence for Zinc-Chromium Duplex
Plating When Chromium was Plated First

- (1) Alkaline clean, anodic, 1 minute, 50 ASF.
- (2) Hot-water rinse.
- (3) Acid dip, 3 N H_2SO_4 , 30 seconds, 80°F.
- (4) Cold-water rinse.
- (5) Chromium plate.
- (6) Hot-water rinse.
- (7) Zinc strike.
- (8) Cold-water rinse.
- (9) Zinc plate.

Cadmium-Chromium. The plating solutions, conditions, and finishing sequences for the cadmium-chromium duplex plating are given in this section.

Cadmium-Plating Solution

Cadolyte single salt*	120 g./l.
Temperature:	80°F.
Current Density:	25 ASF
Anodes:	Steel

*The Udylyte Corporation, Detroit 11, Michigan.

Chromium-Plating Solution

CrO_3	250 g./l.
SO_4	2.5 g./l.
Temperature:	120°F.
Current Density:	225 ASF
Anodes:	Antimonial lead.

Finishing Sequence for Cadmium-Chromium Duplex Plating

- (1) Alkaline clean, anodic, 1 minute, 50 ASF.
- (2) Hot-water rinse.
- (3) Acid dip, 3N H_2SO_4 , 30 seconds, 80°F.
- (4) Cold-water rinse.
- (5) Ten seconds dip in 10% NaCN solution, 70°F.
- (6) Cold-water rinse.
- (7) Cadmium plate.
- (8) Cold-water rinse.
- (9) Chromium plate.

Manganese-Cadmium. The plating solutions, conditions, and finishing sequence for the manganese-cadmium duplex plating are given in this section.

Table 19 contains data for the preparation of some typical specimens.

TABLE 19. SOME EXAMPLES OF THE PREPARATION OF
MANGANESE-CADMIUM DUPLEX COATINGS

Specimen Number	Manganese Plating			Cadmium Plating			Remarks
	Temp. (°F.)	Amps.	C.D. Time (Min.)	Temp. (°F.)	Amps.	C.D. Time (Min.)	
5486 - 92C	98	1.9	45	90	0.75	18	4.9 Satisfactory duplex plate,
- 92E	100	1.9	"	90	0.75	"	4.9 Ditto
- 92F	100	1.9	"	90	0.75	"	4.9 "
- 92G	100	1.9	"	90	2.0	"	1.84 Cadmium plate blistered.
- 92J	98	1.9	"	90	0.75	"	4.9 Satisfactory duplex plate.
- 92K	100	1.9	"	90	1.0	"	3.7 Cadmium plate blistered on one side.

Manganese-Plating Solution

$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	40 g./l.
$(\text{NH}_4)_2 \text{SO}_4$	135 g./l.
$\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$	0.5 g./l.
Temperature:	100°F.
Current Density:	1.5 ASF
Anodes:	Carbon rods in Alundum cups
Anolyte:	$(\text{NH}_4)_2 \text{SO}_4$ 135 g./l.
pH:	7.5

Cadmium-Plating Solution

Cadolyte single salt*	120 g./l.
Temperature:	80°F.
Current Density:	30 ASF
Anodes:	Steel

Finishing Sequence for Manganese-Cadmium Duplex Plating

- (1) through (7) Same as for manganese-zinc.
- (8) Cadmium plate.
- (9) Rinse and dry.

* The Udylite Corporation, Detroit 11, Michigan.

Zinc-Silver Codeposition

Small portions of solution, usually 100 ml., were used in the zinc-silver codeposition experiments. The usual apparatus, consisting of variable rheostat, ammeter, voltmeter, etc., was used. The solutions were contained in a beaker and were heated by immersion in a thermostatically controlled water bath.

Table 20 contains the details of experiments in the iodide solution. The details of the composition and operating conditions for the thiosulfate solution are given below.

Thiosulfate Solution and Conditions for Zinc-Silver Electrodeposition

$\text{Na}_2\text{S}_2\text{O}_3$ (anhyd.)	200 g./l.
AgNO_3	3.6 g./l.
$\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$	0.36 g./l.
ZnCl_2	35 g./l.
H_2SO_4 (Sp. Gr. 1.85)	0.36 ml./l.

Solution used with agitation and with or without 2 g./l. gelatin.

Anode:	Carbon
Cathode:	Stainless steel
Current Density:	18 ASF
Temperature:	70°F.

TABLE 20. ZINC-SILVER ALLOY PLATING EXPERIMENTS (IODINE SOLUTION)

Test Number	Bath Composition	Temperature (°F.)	Current Density (Amps./Sq. Ft.)	Volts	Time (Min.)	Anode	Cathode	Results
4557 - 9A	NaI 520 g./l. Citric acid 60 g./l. ZnI ₂ 394 g./l. Ag ₂ O 2.5 g./l.	85	8.8	1.35	4	Carbon	Stainless steel	Powdery surface. Underlying deposit adheres fairly well and is compact.
- 9B	Ditto	177	8.8	0.97	10	Ditto	Ditto	Powdery deposit rubs off easily.
- 9C	Ditto + 1 g./l. Naphthalene 1, 5, - Disulfonic acid	91	8.8	1.35	4	"	"	Same as 9A.
- 9D	Ditto	90	8.8	1.2	-	"	SAE 1010	Better than 9A, 9B, or 9C. Deposit had a silver mat color. Less powdery.
- 10A	"	88	8.8	1.4	3	"	Brass	Dark plate. Powdery surface.
- 10B	"	88	70.0	2.75	6	"	Stainless steel	Gray plate. Powdery surface. 3% silver.
- 10C	"	89	35.0	1.95	12	"	Ditto	Dark gray plate. Powdery surface. 7.5% silver.
- 10D	"	89	10.0	1.25	26	"	"	Dark gray plate. Powdery surface. 38% silver.
3363 - 58A	Same as 4557 - 9A	70	5.0	1.23	64	"	"	Gray deposit. Powdery surface. 50.3% silver. (Note: This experiment differed from the three preceding, in that there was no addition agent and the temperature was lower. It is included as a fourth point for Figure 1.
4557 - 12A	Ditto	90	20.0	1.55	10	"	"	Powdery surface. Underlying surface is sound. About 0.25 mil thick.
- 12B	Ditto + 1 g./l. Beta naphthol	90	20.0	1.52	10	"	"	Ditto
- 12C	12B + thiourea	90	20.0	1.55	10	"	"	Ditto, but outer layer darker and thicker.
- 12D	12C + carbon disulfide	85	20.0	1.6	10	"	"	Same as 12A and 12B.

TABLE 20. (Continued)

Cast Number	Bath Composition	Temperature (°F.)	Current Density (Amps./Sq.Ft.)	Volts	Time (Min.)	Anode	Cathode	Result
4557 - 12B	12C + 5 ml. H ₂ O	85	20.0	-	10	Carbon	Stainless steel	White deposit. Heavier gassing. Positive test for silver. Negative test for zinc.
- 13A	Same as 4557 - 9A	40	20.0	1.75	10	Ditto	Ditto	Hard nodular plate, part of which scraped off easily. Dark gray. Silver and zinc present. Some improvement over higher temperature.
- 13B	Ditto + beta naphthol	40	20.0	1.77	10	"	"	Medium gray plate. Less powdery.
- 13C	13B + resorcinol	40	20.0	1.77	10	"	"	Ditto
- 13D	Ditto	40	20.0	1.75	10	"	"	Agitated mildly. No improvement.
Agitation, supplied by a magnetic stirrer, was used in the following experiments.								
- 14A	Same as 4557 - 9A	85	20.0	1.53	10	"	"	Medium agitation. No improvement over still solution.
- 14B	Ditto	85	20.0	1.53	7	"	Brass	Medium agitation. No improvement.
- 14C	Ditto + beta naphthol	85	20.0	1.53	10	"	Stainless steel	Ditto
- 14D	14C + resorcinol	85	20.0	1.53	10	"	Ditto	"
- 14E	Ditto	85	20.0	1.53	10	"	"	Rapid agitation. No improvement.
- 14F	"	85	10.0	1.35	20	"	"	Slimy deposit. Looked like silver. Medium agitation, immersion deposit.
- 20A	Same as 4557 - 9A	80	100.0	4.5	5	"	"	Black powdery deposit.

TABLE 23. PRELIMINARY MANGANESE-TIN ELECTRODEPOSITION EXPERIMENTS

Test Number	Bath Type and Number	Bath Composition	Temp. (°F.)	Current Density (Amps./Sq.Ft.)	Time (Min.)	pH	Anode	Cathode	Results	Additions to Bath at End of Test
5022 - 5A	6A Pyrophosphate	$K_4P_2O_7 \cdot 3H_2O$ $MnSO_4 \cdot H_2O$ 230 g./l. 40 g./l.	78	40	75	8.0	Lead-silver alloy 99% Pb-1% Ag	Stainless steel	Positive test for manganese, trace of tin.	50 ml. $Sn-K_4P_2O_7$ solution
- 5B		Na_2SO_3 (.005 g./ml.) 50 g./l.	78	40	30	"	Ditto	Ditto	Trace of tin, no manganese.	50 g. $MnSO_4 \cdot H_2O$ 200 g. $K_4P_2O_7 \cdot 3H_2O$
- 5C		$Sn-K_4P_2O_7$ solution. $K_4P_2O_7 \cdot 3H_2O$ $SnSO_4$ 300 g./l. 55 g./l. 1 g./l.	78	75	10	"	"	"	Positive test for manganese, trace of tin.	50 ml. $Sn-K_4P_2O_7$ solution
- 5D		Beta naphthol Hide glue 2 g./l. Adjust pH from 9.5 to 8.0 with H_2SO_4	78	144	10	"	"	"	Ditto	Ditto
- 5E			80	72	60	"	"	"	Trace of manganese, trace of tin.	
5022 - 9A	Ammonium thiocyanate	$MnSO_4 \cdot H_2O$ $(NH_4)_2SO_4$ NH_4SCN 76 g./l. 75 g./l. 60 g./l. 4.5 g./l.	78	150	45	-	Lead-silver alloy 99% Pb-1% Ag	Stainless steel	Thin, black, nonadherent deposit Heavy indication of manganese, trace of tin.	4.5 g./l. $MnSO_4$ added
- 11B		Beta naphthol Gelatin Cresol 1.0 g./l. 3.0 g./l. 10 ml./l.	78	150	10	4.6	Ditto	Ditto	Black, thin, adherent deposit. Trace of manganese and trace of tin.	
- 11C			78	144	5	4.6	"	"	Black, thin, adherent deposit. Positive indication of manganese, trace of tin.	
- 11D			78	250	10	4.6	"	"	Top portion of deposit mat color, bottom rough, black. Same analysis as above.	
- 11E			78	43	30	4.7	"	"	Thin black deposit. Trace of manganese, trace of tin.	
- 11F			78	288	30	3.6	"	"	Rough, black deposit. Positive indication of manganese, trace of tin.	
- 11G			78	144	20	3.6	"	"	Black, porous, nonadherent top layer. Thin, dark, adherent deposit underneath. Positive indication of Mn. Trace of Sn.	
- 11H			78	43	30	3.6	"	"	Thick sponge tin layer, nonadherent. Thin, black, adherent deposit below. Trace of manganese, trace of tin.	

Manganese-Tin Codeposition

One liter portions of the solutions were used in the manganese-tin codeposition experiments. Again, the usual type of apparatus was used.

Tables 21 and 22 give the experimental details for this work.

Manganese-Nickel Codeposition

The solutions and conditions used in the manganese-nickel codeposition experiments are given below.

Solutions and Conditions Used for Manganese-Nickel Codeposition Experiments

Ammonium Sulfate Type

<u>Solution A.</u>	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	40 g./l.
	$(\text{NH}_4)_2\text{SO}_4$	132.5 g./l.
	$\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$	0.25 g./l.
	pH adjusted to 7.5 with 1-1 NH_4OH	

<u>Solution B.</u>	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	50 g./l.
--------------------	---	----------

<u>Plating Solution.</u>	Solution A	200 ml.
	Solution B	5 ml.

<u>Plating Conditions.</u>	Anode:	Carbon
	Cathode:	Stainless steel

TABLE 2. ANALYSIS OF PLATING SOLUTIONS

No.	Date	Time	Analysis of		Cell	Results
			Weight	Volume		
17A	10/10/50	10:00	100	100	100	100
17B	10/10/50	10:00	100	100	100	100
17C	10/10/50	10:00	100	100	100	100
17D	10/10/50	10:00	100	100	100	100
17E	10/10/50	10:00	100	100	100	100
17F	10/10/50	10:00	100	100	100	100
17G	10/10/50	10:00	100	100	100	100
17H	10/10/50	10:00	100	100	100	100
17I	10/10/50	10:00	100	100	100	100
17J	10/10/50	10:00	100	100	100	100
17K	10/10/50	10:00	100	100	100	100
17L	10/10/50	10:00	100	100	100	100
17M	10/10/50	10:00	100	100	100	100
17N	10/10/50	10:00	100	100	100	100
17O	10/10/50	10:00	100	100	100	100
17P	10/10/50	10:00	100	100	100	100
17Q	10/10/50	10:00	100	100	100	100
17R	10/10/50	10:00	100	100	100	100
17S	10/10/50	10:00	100	100	100	100
17T	10/10/50	10:00	100	100	100	100
17U	10/10/50	10:00	100	100	100	100
17V	10/10/50	10:00	100	100	100	100
17W	10/10/50	10:00	100	100	100	100
17X	10/10/50	10:00	100	100	100	100
17Y	10/10/50	10:00	100	100	100	100
17Z	10/10/50	10:00	100	100	100	100
18A	10/10/50	10:00	100	100	100	100
18B	10/10/50	10:00	100	100	100	100
18C	10/10/50	10:00	100	100	100	100
18D	10/10/50	10:00	100	100	100	100
18E	10/10/50	10:00	100	100	100	100
18F	10/10/50	10:00	100	100	100	100
18G	10/10/50	10:00	100	100	100	100
18H	10/10/50	10:00	100	100	100	100
18I	10/10/50	10:00	100	100	100	100
18J	10/10/50	10:00	100	100	100	100
18K	10/10/50	10:00	100	100	100	100
18L	10/10/50	10:00	100	100	100	100
18M	10/10/50	10:00	100	100	100	100
18N	10/10/50	10:00	100	100	100	100
18O	10/10/50	10:00	100	100	100	100
18P	10/10/50	10:00	100	100	100	100
18Q	10/10/50	10:00	100	100	100	100
18R	10/10/50	10:00	100	100	100	100
18S	10/10/50	10:00	100	100	100	100
18T	10/10/50	10:00	100	100	100	100
18U	10/10/50	10:00	100	100	100	100
18V	10/10/50	10:00	100	100	100	100
18W	10/10/50	10:00	100	100	100	100
18X	10/10/50	10:00	100	100	100	100
18Y	10/10/50	10:00	100	100	100	100
18Z	10/10/50	10:00	100	100	100	100
19A	10/10/50	10:00	100	100	100	100
19B	10/10/50	10:00	100	100	100	100
19C	10/10/50	10:00	100	100	100	100
19D	10/10/50	10:00	100	100	100	100
19E	10/10/50	10:00	100	100	100	100
19F	10/10/50	10:00	100	100	100	100
19G	10/10/50	10:00	100	100	100	100
19H	10/10/50	10:00	100	100	100	100
19I	10/10/50	10:00	100	100	100	100
19J	10/10/50	10:00	100	100	100	100
19K	10/10/50	10:00	100	100	100	100
19L	10/10/50	10:00	100	100	100	100
19M	10/10/50	10:00	100	100	100	100
19N	10/10/50	10:00	100	100	100	100
19O	10/10/50	10:00	100	100	100	100
19P	10/10/50	10:00	100	100	100	100
19Q	10/10/50	10:00	100	100	100	100
19R	10/10/50	10:00	100	100	100	100
19S	10/10/50	10:00	100	100	100	100
19T	10/10/50	10:00	100	100	100	100
19U	10/10/50	10:00	100	100	100	100
19V	10/10/50	10:00	100	100	100	100
19W	10/10/50	10:00	100	100	100	100
19X	10/10/50	10:00	100	100	100	100
19Y	10/10/50	10:00	100	100	100	100
19Z	10/10/50	10:00	100	100	100	100
20A	10/10/50	10:00	100	100	100	100
20B	10/10/50	10:00	100	100	100	100
20C	10/10/50	10:00	100	100	100	100
20D	10/10/50	10:00	100	100	100	100
20E	10/10/50	10:00	100	100	100	100
20F	10/10/50	10:00	100	100	100	100
20G	10/10/50	10:00	100	100	100	100
20H	10/10/50	10:00	100	100	100	100
20I	10/10/50	10:00	100	100	100	100
20J	10/10/50	10:00	100	100	100	100
20K	10/10/50	10:00	100	100	100	100
20L	10/10/50	10:00	100	100	100	100
20M	10/10/50	10:00	100	100	100	100
20N	10/10/50	10:00	100	100	100	100
20O	10/10/50	10:00	100	100	100	100
20P	10/10/50	10:00	100	100	100	100
20Q	10/10/50	10:00	100	100	100	100
20R	10/10/50	10:00	100	100	100	100
20S	10/10/50	10:00	100	100	100	100
20T	10/10/50	10:00	100	100	100	100
20U	10/10/50	10:00	100	100	100	100
20V	10/10/50	10:00	100	100	100	100
20W	10/10/50	10:00	100	100	100	100
20X	10/10/50	10:00	100	100	100	100
20Y	10/10/50	10:00	100	100	100	100
20Z	10/10/50	10:00	100	100	100	100

Stannous sulfate - pyrophosphate solution. $K_2P_2O_7 \cdot 3H_2O$ - 300g./l., beta naphthol - 1.0g./l., pyraline - 2.0 g./l., pH adjusted from 7.5 to 8.0 with H_2SO_4 .

TABLE 21. (Continued)

Test Number	Bath Type and Number	Bath Composition	Temp. (°F.)	Current Density (Amps./sq. ft.)	Time (Min.)	pH	Anode	Cathode	Results	Additions to Bath at End of Test
5022 - 111	Ammonium thiocyanate 5022 - 104		78	57	15	3.6	Lead-silver alloy 99% Pb-1% Ag	Stainless steel	Thick sponge tin layer, nonadherent. Thin, black, adherent deposit below. Trace of manganese, trace of tin.	0.5 g. Na_2SO_3 crystals
- 111J	(Continued)		78	57	15	4.0	Ditto	Ditto	Smooth, thin, dark mat deposit. Positive indication of manganese, trace of tin.	
- 111K			78	288	3	4.0	"	"	Rough, adherent deposit. Positive indication of manganese, positive indication of tin.	Bath filtered
- 111L			78	288 (9 volts)	15	4.0	"	"	Thick black deposit, rough surface adherent. Trace of manganese, positive indication of tin.	
- 111M			78	216 (7 volts)	15	4.0	"	"	Ditto	13 g./l. Na_2SO_3 added
- 111N			78	400	30	4.0	"	"	Black, nonmetallic appearing, adherent deposit. Positive indication of manganese, trace of tin.	
5022 - 13A	Pyrophosphate 5022 - 12A	$\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ 40 g./l. $\text{K}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ 725 ml. of 800 g./l. soln.	78	43	6	8.0	"	"	Continuous, dark mat, smooth, good adherence, 6.3% Mn.	
- 13B		Na_2SO_3 soln. (.005 g./ml.) 50 ml. Add 50 ml./l. of the following soln.	78	144	6	8.0	"	"	Dark, slightly rough, good adherence. 3% Mn.	
- 13C		$\text{K}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ 300 g./l. SnSO_4 55 g./l. Beta naphthol 1 g./l. Gelatin 2 g./l.	78	216	6	8.0	"	"	Black color, rough surface, good adherence. 4.3% Mn.	

TABLE 22. (Continued)

Test Number	Bath No.	Temp. (°F.)	Current Density (Amps./Sq. Ft.)	Time (min.)	pH	Analysis of Deposit		Cell Voltage	Results	Additions to Bath at End of Test
						% Mn	% Sn			
5022-49A	43A	92	24.0	8.0	15	Balance	17.0	7.5	Smooth, adherent, metallic mat gray plate.	
50A	"	"	"	"	"	"	41.0	"	1/2-inch diameter, stainless steel cathode used.	
50B	"	86	"	"	"	"	"	1.2	Smooth, adherent mat gray deposit.	
51A	"	88	"	"	"	"	1.9	"	"	
53A										
Bath composition: $\text{SnSO}_4 \cdot 1.0\text{g./l.}$, tartaric acid-25g./l., hide glue (hydrolyzed solution)-0.1g./l., $(\text{NH}_4)_2\text{SO}_4 \cdot 200\text{g./l.}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O} \cdot 100\text{g./l.}$, $\text{H}_2\text{SO}_4 \cdot 0.5\text{g./l.}$, 3-liter volume.										
5022-54A	53A	80	24.0	7.5	15	Balance	40.76	9.6	Good-appearing mat deposit.	
54B	"	100	"	"	"	"	40.82	7.5	Good deposit, MnO_2 darkened bath.	
54C	"	120	"	"	"	"	40.0	7.5	"	
54D	"	"	"	"	"	"	"	"	"	
55A	"	150	"	"	"	Balance	11.3	"	Good-appearing mat deposit.	
56A	"	"	"	"	"	"	13.4	"	Lower tin content result of 5 hours dummaging.	
56B	"	118	360	7.7	15	"	12.8	8.0	Smooth, adherent mat gray deposit.	
56C	"	118	"	"	"	"	15.2	"	"	
57A										
Bath composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O} \cdot 40\text{g./l.}$, $(\text{NH}_4)_2\text{SO}_4 \cdot 135\text{g./l.}$, $\text{H}_2\text{SO}_4 \cdot 0.16\text{g./l.}$, Modified ammonium stannous oxalate solution* -3.3ml./l.										
5022-57A	57A	115	96	7.5	15	Heavy	None	5.5	Very good deposit, smooth, adherent, mat color.	25 ml. modified ammonium stannous oxalate solution.
58A	"	"	120	7.6	"	"	"	6.0	"	
59A	"	86	132	7.6	15	Heavy	Heavy	6.2	Analysis not completed, tin too high.	Bath became cloudy.
59B	"	92	24.0	"	"	"	"	8.0	"	25 g. tartaric acid added, pH adjusted to 7.5. Cloudiness did not reappear.
60A										
Bath composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O} \cdot 40\text{g./l.}$, $(\text{NH}_4)_2\text{SO}_4 \cdot 135\text{g./l.}$, $\text{H}_2\text{SO}_4 \cdot 0.25\text{g./l.}$, Tartaric acid -8g./l., modified stannous ammonium oxalate solution -3.3 ml./l., 3 liter volume bath.										
5022-60A	60A	90	216	7.8	15	"	"	8.2	Sample lost in furnace during ignition.	
60B	"	120	120	"	"	Balance	9.9	6.8	Smooth mat color deposit.	
60C	"	"	"	"	"	"	8.7	"	"	
61A	"	120	120	8.0	30	Balance	6.4	6.0	Smooth, adherent, mat deposit.	5.0 ml. modified ammonium oxalate solution added to bath.
61B	"	"	"	"	"	"	5.4	"	"	

* Preparation of the modified stannous ammonium oxalate solution: 25g. tartaric acid dissolved in 1 l. distilled water and added to 250 ml. stannous ammonium oxalate solution. If precipitate settles out, dissolve by heating the solution to 100°F., adjust pH to 7.5.

TABLE 22. (Continued)

Test Number	Bath Temp. (°F.)	Current Density (Amps./Sq. Ft.)	pH	Time (Min.)	Analysis of Deposit	Cell Voltage	Results	Additions to Bath at End of Test
5022-29A Bath composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ -40g./l., $(\text{NH}_4)_2\text{SO}_4$ -137 g./l., Na_2SO_3 -0.25g./l., 3-liter volume bath.								
5022-29B	100	72	7.2	45	-	-	Cathode aritated.	SnSO_4 -1.6g./l.
29C	"	"	7.5	60	-	-	Good mat color deposit. S.A.P. 1010 cathode.	
30A	"	100	7.2	30	Balance	1.16	Static plating conditions.	
31A	"	"	"	31.5	"	0.40	Agitation of bath, static cathode.	
32A	"	"	"	30	"	"	Agitation of cathode.	
32B	"	"	"	"	"	"	"	
33A	98	60	7.0	90	Balance	0.20	"	
33B	"	"	"	"	"	0.37	"	
34A	100	100	7.2	30	"	0.40	Removal of test 5022-32A.	
35A Bath composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ -100g./l., $(\text{NH}_4)_2\text{SO}_4$ -75g./l., Na_2SO_3 -0.25g./l., one-liter volume bath.								
5022-35A	100	40	4.0	20	-	-	Four deposit. MnO_2 precipitate in bath.	
35B	100	100	"	"	-	-	"	
36A Bath composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ -40g./l., $(\text{NH}_4)_2\text{SO}_4$ -135g./l., Na_2SO_3 -0.25g./l., ammonium stannous oxalate solution - 20ml. 3-liter volume bath.								
5022-36A	78	75	5.0	10	None	Heavy	Very good appearing mat plate.	40 ml. Ammon. stannous oxalate
36B	"	"	"	15	Trace	"	Gray deposit.	100 ml. Ammon. stannous oxalate
36C	"	"	"	"	"	"	Very poor black deposit	Solution boiled 1-1/2 hours with sponge tin.
36D	140	75	-	15	None	Heavy	Smooth tin deposit.	
39A Bath composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ -40g./l., $(\text{NH}_4)_2\text{SO}_4$ -135g./l., Na_2SO_3 -0.25g./l., tartaric acid - 25 g./l., hydrolyzed hide glue solution - 0.1 g./l., 3-liter volume bath.								
5022-40A	145	72	8.0	30	Balance	72	4.2	
40B	"	50	8.0	40	"	59	3.7	
41A	"	24	7.8	60	"	65	3.2	
42A	"	72	"	10	"	42	"	
42B	"	50	"	15	"	44	"	
43A Bath composition: $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ -50g./l., $(\text{NH}_4)_2\text{SO}_4$ -135g./l., Na_2SO_3 -1.0g./l., tartaric acid-25g./l., hydrolyzed hide glue solution -0.1g./l., 3-liter volume bath.								
5022-45A	120	100	7.5	15	Balance	39.0	-	
46A	"	370	8.0	10	"	49.0	2.5	
46B	92	360	8.4	15	"	34.6	9.0	
47A	"	240	8.2	15	"	35.8	8.2	
48A	80-90	"	-	15	-	-	-	
48B	95	"	-	30	-	-	-	

1. Na_2SO_3 - 50g./l.
 2. $(\text{NH}_4)_2\text{SO}_4$ - 45g./l.
 3. Na_2SO_3 - 0.25g./l.

* Ammonium stannous oxalate solution: Composition and details of preparation: 50g. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in HCl solution. Stannous oxalate precipitated by adding 30 g. H_2O - CCl_4 dissolved in H_2O . Precipitate washed thoroughly and dried. A mixture composed of 50 g. dried stannous oxalate, 10 g. $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ dissolved in H_2O and 15g. H_2O in H_2O . To this was added 50 ml. of a hydrolyzed hide glue solution prepared by boiling 2g. hide glue in 400 ml. H_2O for 1 hour.

Current Density:	40 ASF
Volts:	3.5
Temperature:	90°F.

Pyrophosphate Type

Solution A. $\text{MnSO}_4 \cdot \text{H}_2\text{O}$	400 g./l.
Solution B. $\text{K}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$	800 g./l.
Solution C. $\text{Na}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	50 g./l.

<u>Plating Solution.</u>	Solution A	10 ml.
	Water	100 ml.
	Solution B	50 ml.
	Solution C	5 ml.

<u>Plating Conditions.</u>	Anode:	Carbon
	Cathode:	Stainless steel
	Current Density:	40 ASF
	Volts:	3.7
	Temperature:	120°F.
	pH not measured	

Zinc-Tin Alloy Plating

This bath has been described by Guthbertson*. For convenience, the bath formula and plating conditions are given here. In addition, several necessary precautions are mentioned.

*J. Electrochem. Soc. 94, 73 (1948).

Zinc-Tin Alloy-Plating Solution

Tin (as sodium stannate)	30 g./l.
Zinc (as zinc cyanide)	2.5 g./l.
Sodium hydroxide (free)	4-6 g./l.
Total cyanide*	25-28 g./l.
Free sodium cyanide	17.5 g./l.
Temperature:	140°F.
Anodes:	Cast 20% zinc - 80% tin alloy.
Current Density:	25 ASF

Note: High-purity sodium stannate must be used. For commercial units, a special grade is procurable from Metal and Thermit Corp., Rahway, N. J. For experimental solutions, the C. P. stannate made by the J. T. Baker Chemical Co., Phillipsburg, N. J., is suitable.

The bath should be made up as follows: fill the container to two-thirds of its volume with water, preferably distilled or softened, and heat to 140°F. Dissolve sodium cyanide, sodium hydroxide, and zinc cyanide, in that order. Finally add sodium stannate. Analyze the solution and adjust the components.

It is well to hold the bath at 140°F. for 2-3 days before plating.

Literature on the bath can be obtained from the Tin Research Institute, Inc., 492 W. Sixth Avenue, Columbus 1, Ohio.

*Expressed as sodium cyanide.

Experimental Zinc-Lead Alloy Fluoborate Solution

Solution A: (Concentrate as supplied by
General Chemical Co.)

$\text{Zn}(\text{BF}_4)_2$	50.45% (by weight)
Free H_3BO_3	3.54%

Solution B: (Concentrate as supplied by
General Chemical Co.)

$\text{Pb}(\text{BF}_4)_2$	50% (by weight)
Free HBF_4	0.7%
Free H_3BO_3	4.0%

Solution 4557 - 90A

Solution A	100 ml.
Solution B	10 ml.
Hide Glue (40 g./l.)	2 ml.
Dilute to 400 ml.	

Temperature: 80° - 120°F.

Current Density: 10 - 40 ASF

pH: 0.0 (paper)

Results: Spongy deposit containing only lead.

Experimental Zinc-Lead Alloy
Zincate-Plumbite Solution

Zincate Stock Solution

ZnCl ₂	75 g./l.
NaOH	255 g./l.
Rochelle Salt	35 g./l.

Zincate-Plumbite Solution

Zincate Stock Solution 400 ml.

Pb(OH)(C₂H₃O₂)₃ 1 g.

RH 774* 0.5 ml.

Temperature: 74°F.

Current Density: 10 ASF

Result: Spongy deposit containing lead only.

Zinc-Lead-Plating Solution

ZnCl₂ 1000 g.

H₂O 500 g.

PbCl₂ 20 g.

Temperature: 170°F.

Current Densities: See Table 23

Anodes: Platinum

* E. I. du Pont de Nemours Co., Wilmington, Del.

TABLE 23. PRELIMINARY EXPERIMENTS ON THE
COMPOSITION OF ZINC AND LEAD

Specimen Number	Temp. (°F.)	Amps.	C.P. (.5F)	Time (Mins.)	Agitation	Weight of Coating (Grams)	Remarks
- 11A	170	0.15	10.7	10	No	0.095	Deposit is dark, spongy, bread, and non-adherent.
- 11B	170	0.034	2.4	40	No	0.083	Same as 11A but less treading and better adherence. 94.9% Pb.
- 11C	170	0.14	5	20	Yes*	0.081	Crystalline deposit, somewhat tread, but not spongy. Loosely adherent. 97.6% Pb.
- 11D	170	0.036	1.25	80	Yes*	0.088	Fine crystalline deposit. Less tread than 11C. Loosely adherent. 85.4% Pb. A subsequent test showed that all the lead was not precipitated.

* Cork-rod agitation, 1-1/4-inch stroke, 64 strokes/min.

In preparing the zinc-lead chloride solution, the lead chloride was not so readily soluble as it was in lithium chloride solution. It was necessary to keep the solution hot in order to prevent precipitation. It may be that the material which precipitates when the solution cools is not pure lead chloride, but is a complex such as ZnPbCl_4 .

Cadmium-Silver Plating

Cd O	32 g./l.
AgCN	2.1 g./l.
NaCN	83 g./l.
Na_2CO_3	10 g./l.
$\text{NH}_4\text{OH}(28\%)$	2 ml./l.
Free sodium cyanide	32 g./l.
Temperature:	90°F.
Current Density:	21 ASF
Voltage:	2.2 volts
Anodes:	Steel
Analysis of Deposit:	7.4% silver

Iron-Chromium Alloy Plating

A complete description of the process for plating iron-chromium alloys will be found in the Final Technical Report entitled "A Research Investigation of Possibilities for Obtaining Hot-Hard Electrodeposited Chromium or Chromium-Base Alloys for Cannon" (restricted). This work was done for the Army Ordnance Department under Contract #33-019-ORD-6397.

Zinc-Nickel ("Corronized") Coatings

Panels coated with several zinc-nickel alloys were supplied free of charge by the Standard Steel Spring Company, Coraopolis, Pa.

Nitriding of the Steel Panels

The 1-inch by 4-inch SAE 4130 panels were placed in a tube furnace, ammonia was passed through the furnace, and the temperature was raised to 975°F. This temperature was maintained for four hours. The specimens were then cooled in the furnace in the ammonia atmosphere. The surfaces had the dull-gray appearance characteristic of a nitrided surface. Scratch testing showed the surfaces to have been hardened.

Preparation of Four-Inch by Six-Inch Steel Panels

The SAE 4130 steel used for these panels measured 4 inches by 18 inches by 1/32 inch as received. Before cutting to the desired size of 4 by 6 inches, the steel was cleaned and polished. The larger size permitted easier polishing.

The panels were cleaned in a hot, alkaline, soak cleaner. They were then polished on 240-grit, substantially new, emery belts. The final finish was with a sisal buff (Tampico wheel). This resulted in a finish about equivalent to a 300 grit. The panels were then cut to the 4-inch by 6-inch size, care being taken not to mar the surfaces. The panels were stored under kerosene until ready to plate.

Description of Plating Racks for Four-Inch by Six-Inch Panels

The so-called "robber" was formed from 1/8-inch by 1-inch hot-rolled, plain-carbon steel. The robber was bent into a rectangular frame measuring $6\frac{1}{2}$ inches by $4\frac{1}{2}$ inches, inside dimensions. The two ends of the frame were welded together. The steel panel is supported within this frame by three contact points. Two of these are located on the inside of the lower $4\frac{1}{2}$ -inch section and are rigid. The third is a spring clip located at the upper $4\frac{1}{2}$ -inch section. A rod is brazed, end on, to the outside of the upper $4\frac{1}{2}$ -inch section. The rack is suspended in the bath by this rod. Figure 7 is a photograph of the plating rack, with a 4-inch x 6-inch panel in place.

A slight modification of the rack was necessary in order to get good distribution when plating manganese. The one-inch-wide strip was narrowed to three-quarters inch, and four quarter-inch holes were drilled in the top strip to allow the gas to escape.

The plating solutions and finishing sequences used in preparing the outdoor panels have been described earlier in this section.

Three thicknesses, 0.1 mil., 0.3 mil., and 0.5 mil., were prepared for each type of coating and four panels for each thickness. The Magne-Gage was used for determining thickness. A tolerance of $\pm 10\%$, relative to the nominal thicknesses given above was allowed. The magnets that were available were calibrated for manganese plate.

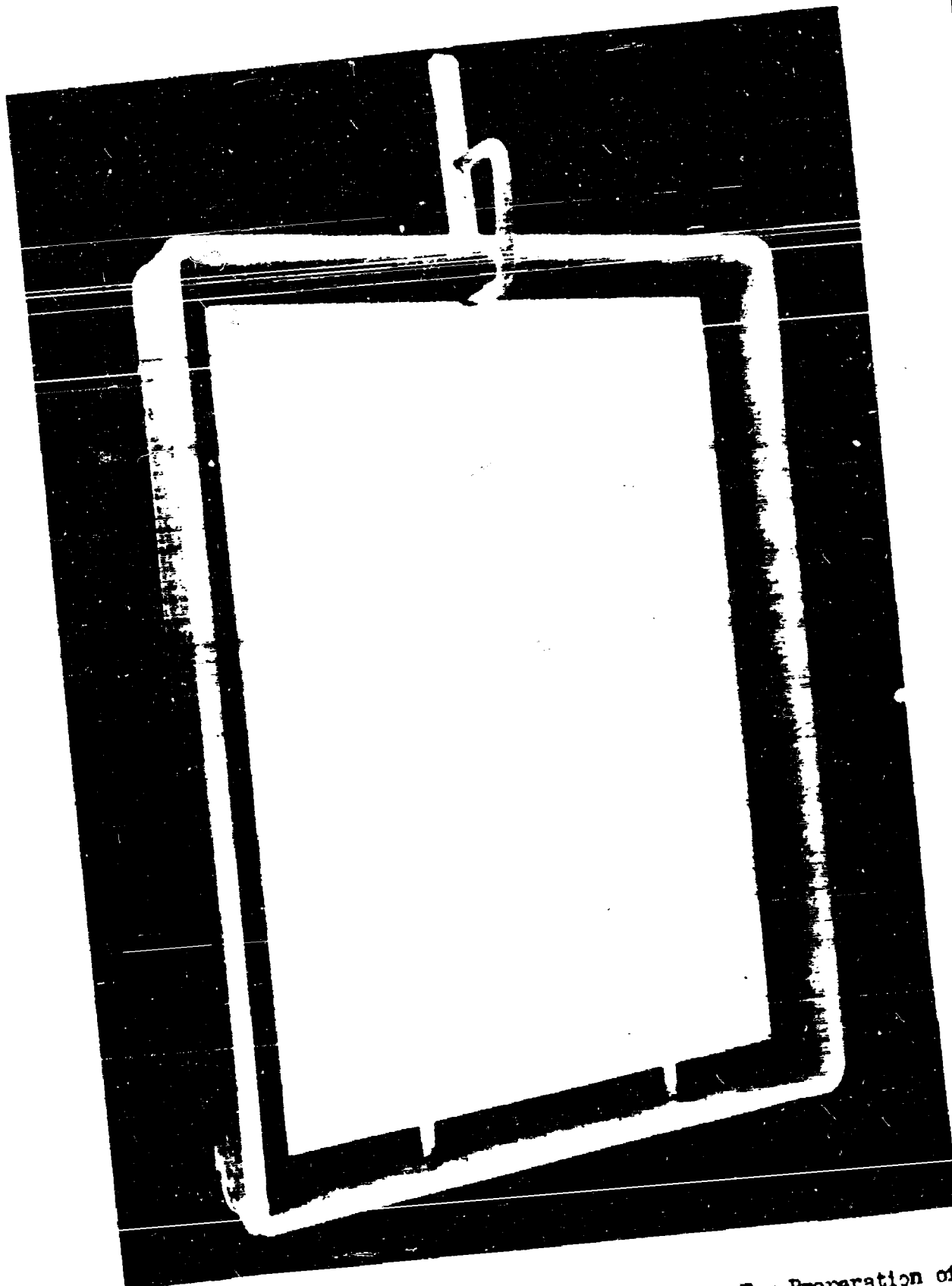


Figure 7. "Robber" Type Plating Rack, Used For Preparation of 4
Inch x 6-Inch Outdoor Exposure Panels.

APPENDIX II

This Appendix contains tabulated data on the "wet-dry" tests, and the X-ray diffraction photograms.

TABLE 24. DETAILED RESULTS OF WENT-UNO² EXPOSURE TEST

Type Coating	Composition (Weight %)	Specimen Number	Coating Thickness (mils)	Scratched	Cycles to First Rust	Cycles to Total Cycles	Final Average of Specimen
Zn - Ag (Cast)	7.95% Ag	2875-60C1	--	--	--	100	
		60C2	--	--	--	100	
	1.04% Ag	60B1	--	--	--	100	
		60B3	--	--	--	100	
	1.24% Ag	60A1	--	--	--	100	
		60A2	--	--	--	100	
Zn (Cast)	100% Zn	2875-50A	--	--	--	100	
		3180-197	--	--	--	100	
	7.35% Ag	3363-93A	0.25	No	2	No	
		3363-93C	0.25	Yes	2	•	
Zn - Ag (Electroplate)		3363-93D	0.25	No	2	•	
		3363-93F	0.25	Yes	2	•	
	100% Cd	56B	0.3	No	No rust	•	
		56D	0.3	No	?	•	
Zn + Sn overlay		86E	0.26 Mn + .06 Sn	No	No rust	•	
		86F	0.26 Mn + .03 Sn	No	Diff	•	
		86G	0.26 Mn + .06 Sn	No	•	•	

Weight-loss measurements were made on these specimens. See Table 13.

54 rust plus very small amount of white corrosion product.

10% rust. Two-thirds of the rusting was along the scratches.

Less than 2% rust, plus small amount of white corrosion product.

10% rust. One-half the rusting was along the scratches.

One rust spot. Less than 1%.

Less manganese corrosion product; than 1% white corrosion product.

Not quite as good as 86F or 86G but better than 86E manganese.

Same as with 86F.

TABLE 25. DETAILED RESULTS OF WET-DRY* EXPOSURE TEST

Type Coating	Composition (Weight %)	Specimen Number	Coating Thickness (Mils)	Scratched	Cycles To First Rust	Progress of Rusting After Initial Appearance	Total Cycles	Final Appearance of Specimens
Cd - Sn (Diffusion)	50 - 50	3393-66C	0.43	No	8	Very Slow	134	3 small rust areas.
	Ditto	-66F	0.43	Yes	10	Very Slow	134	Slight rusting in scratches near intersection.
	"	-66G	0.35	No	36	Ditto	134	2 very small rust spots.
	"	-66I	0.36	Yes	8	"	134	Rusting in scratches 50% more than 3393-66F.
Cd - Sn (Plated From Sulphuric Solution)	50 - 50	3393-54J	0.05	Yes	2	Rapid	94	90% of surface rusted.
	Ditto	-66K	0.08	No	10	Rapid	94	50% of surface rusted.
	"	-44I	0.3	No	Did Not Rust	----	134	No rust. Coating slightly darker than originally.
	"	-66M	0.15	Yes	22	Slow	134	3 to 5% rust along scratches.
Zn - Ag (Diffusion) (Silver Plated First)	23-25% Ag	4457-45A	0.3	No	4	Very Rapid	78	80% covered with heavy rust.
	Ditto	-75B	0.3	Yes	2	Ditto	78	75% covered with heavy rust.
	"	-75C	0.3	Yes	4	"	78	Ditto
	"	-75I	0.3	No	4	"	78	65% covered with heavy rust.
Zn - Ag (Diffusion) (Zinc Plated First)	23-25% Ag	-68T	0.3	No	2	"	56	80% covered with heavy rust.
	Ditto	-68E	0.3	No	4	"	56	Ditto
	42% Sn	-66C	0.3	No	22	Slow	134	15% iron rust. 10% no corrosion. 75% medium manganese corrosion products.
	"	-66I	0.3	Yes	Did Not Rust	----	134	10% no corrosion. 90% light to medium manganese corrosion products.
Mn - Sn (Diffusion) (Manganese Plated First)	"	-66I	0.3	No	2	Slow	134	50% iron rust. 10% no corrosion. 40% medium manganese corrosion products.

TABLE 25. (Continued)

Type (Salt)	Composition (Weight %)	Specimen Number	Coating Thickness (mils)	Attached First Rust	Cycles To First Rust	Progress of Rusting After Initial Appearance	Total Cycles	Final Appearance of Specimens
Mn - Si (Fickusion) (Manganese Plated First)	2% Sn	4557-84G	0.3	Yes	100	Slow	134	5% iron rust, 10% no corrosion, 85% medium range, in corrosion products.
W	-----	-84B	0.3	No	No Iron Rust	-----	134	Entire surface covered with medium to heavy brown manganese-type corrosion products.
	-----	-85C	0.3	No	No Iron Rust	-----	134	Entire surface covered with medium to heavy brown manganese-type corrosion products.
Sn	-----	-78A	0.3	No	100	Slow	134	Note: The surfaces of these specimens were completely covered with brown corrosion products after two cycles.
	-----	-78B	0.3	No	78	Slow	134	White powdery corrosion products covering 90% of surface. 4% of surface shows rust.
	-----	-79A	0.3	No	No Iron Rust	-----	134	White powdery corrosion products covering 95% of surface, but more bulky than 4557-78A. 15% of surface shows rust.
	-----	-79B	0.3	No	No Iron Rust	-----	134	80% of surface covered with dry green-brown, compact corrosion product which appears to outline grains.
	-----	-79C	0.3	No	No Iron Rust	-----	134	5% of surface as 4557-78A.

TABLE 26. DETAILED RESULTS OF "WET-DRY" EXPOSURE TEST

Type Coating	Composition (Weight %)	Specimen Number	Coating Thickness (Mils)	Scratched	Cycles to First Rust	Progress of Rusting After Initial Appearance	Total Cycles	Final Appearance of Specimen
Uncoated	50 - 50	5177-48V	0.3	No	32	Slow	128	About 30 rust spots covering $\frac{1}{2}$ - 1% of total area. Medium white corrosion products.
"	" - 50	-48J	"	No	12	Very slow	128	Ditto
"	75.5% Ni	-48H	"	No	14	Slow	128	40% rust. Some white corrosion products.
"	77.5% Ni	-48I	"	Yes	1	Slow	128	Ditto
"	77.5% Ni	-48N	"	No	12	Slow	128	"
"	77.5% Ni	-48N	"	Yes	8	Slow	128	20% rust. Some white corrosion products.
"	75% Ni	-48M	"	No	4	Rapid	58	70% rust.
"	75% Ni	-48E	"	Yes	1	Very rapid	58	40% rust.
"	75% Ni	-48C	"	No	8	Rapid	58	80% rust.
"	5% Ni	-48L	"	Yes	1	Rapid	58	80% rust.
"	25% Al	-48B	"	No	1	Very rapid	58	80% heavy rust.
Chromate, Silver Plated (Pines)								
Ditto	25% Al	-48C	"	No	1	Rapid	58	Ditto
"	25% Ag	-48I	"	No	1	Rapid	58	"
"	25% Ag	-48I	"	No	1	Rapid	58	"
Zn	100% Zn	4557-78F	"	No	60	Slow	284	35% rust. Balance of area covered with white corrosion products.
"	100% Zn	-78F	"	No	46	Slow	284	Ditto
"	100% Cd	-79C	"	No	Did not rust	--	284	40% rust. Slight discoloration.
"	100% Cd	-79C	"	No	Ditto	--	284	Ditto

TABLE 26. (Continued)

Type Coating	Corrosion (Weight %)	Specimen Number	Coating Thickness (Mils.)	Scratched	Cycles to First Rust	Progress of Rusting After Initial Appearance	Total Cycles	Final Appearance of Specimen
Zn-Ag (Diffused, silver plated first)	25% Ag	5327-43P1	0.3	No	2	Rapid	24	50% rust
Ditto	Ditto	-43C1	"	No	2	"	24	50% rust
"	"	-39A2	"	No	2	"	24	100% rust
"	"	-39B2	"	No	2	"	64	50% rust
"	"	-39C	"	No	2	"	24	60% rust
"	"	-39E	"	No	2	"	24	60% rust
Mn-Zn (Diffused, Zn plated first)	50% Mn	5286-26E	"	No	118	Slow	128	1% rust. Blue-gray-brown corrosion products. Light gray spots, probably zinc corrosion products, distributed evenly over surface. Corrosion products more adherent and less bulky than those of pure manganese and zinc.
Ditto	50% Mn	-34B	"	No	76	"	128	5% rust. Blue-gray corrosion products. Mn adherent than those from pure manganese.
"	50% Mn	-34C	"	No	118	"	228	5% rust, otherwise same as 26E.
"	75% Mn	-36P	"	No	Questionable	"	72	Ver. much like pure manganese, but not so dark. Corrosion products are powdery and non-adherent.
Mn-Zn (Diffused, Zn plated first)	50% Mn	-34P	"	No	Questionable	"	128	Possibly 5% scattered rust. Color like pure manganese.
Fe-Cr (Codeo-sited)	9% Cr	5351-35B	"	No	2	Rapid	24	50% rust

TABLE 26. (Continued)

Type Coating	Composition (Weight %)	Specimen Number	Coating Thickness (Mil.)	Scratched	Cycles to First Rust	Progress of Rusting After Initial Appearance	Total Rusting Cycles	Final Appearance of Specimen
Pb-Cr (concentrated)	95% Cr	5351-75C	0.3	No	2	Rapid	24	50% rust
Ditto	Ditto	-35G	"	No	2	"	64	Little
"	"	-35G	"	No	2	"	64	"
Zinc	100% Cr	5351-34A	"	No	2	"	64	10% rust
Ditto	Ditto	-34B	"	No	2	"	24	40% rust
Zn (Fluoroborate)	100% Pb	5486-99A	"	No	4	"	64	50% rust
Ditto	Ditto	-99B	"	Yes	4	"	64	Ditto
"	"	-99C	"	Yes	4	"	64	"
"	"	-99D	"	No	4	"	64	"

1. Diffused 4 hours at 603°F. in a hydrogen atmosphere.
2. Diffused 4 hours at 1000°F. in a hydrogen atmosphere.

TABLE 27. DETAILED RESULTS OF "WET-DRY" EXPOSURE TEST

Type Coating	Composition (Weight %)	Specimen Number	Coating Thickness (mils)	Scratched	Exposed to Rust	Cycles to 50% Rust	Index	Remarks
Mo-Zr (Diffused)	25% Mo	5486-76C	0.3	No	6	68	365	
		76D	Ditto	No	6	70	350	
		72E	"	No	66	212	1377	
		68F	"	No	2	212	1191	
		76H	"	Yes	2	108	614	
75% Mo	100% zinc	76G	"	Yes	2	150	830	Rust spots less visible at 1/2 cycles. No bare areas at 3/4 cycles.
		76F	"	No	6 (7)	Over 222	1528	
		74G	"	No	6	164	846	
		5351-53E	"	Yes	34	82	490	
		53F	"	No	20	66	417	
Zn on nitrided steel	100% zinc	53G	"	Yes	40	86	479	
		53H	"	No	26	78	460	
		53A	"	Yes	20	78	442	
		53B	"	No	20	66	409	
		53C	"	Yes	20	82	442	
Zn on plain steel	100% zinc	53D	"	No	20	78	461	
		53E	"	No	20	78	461	

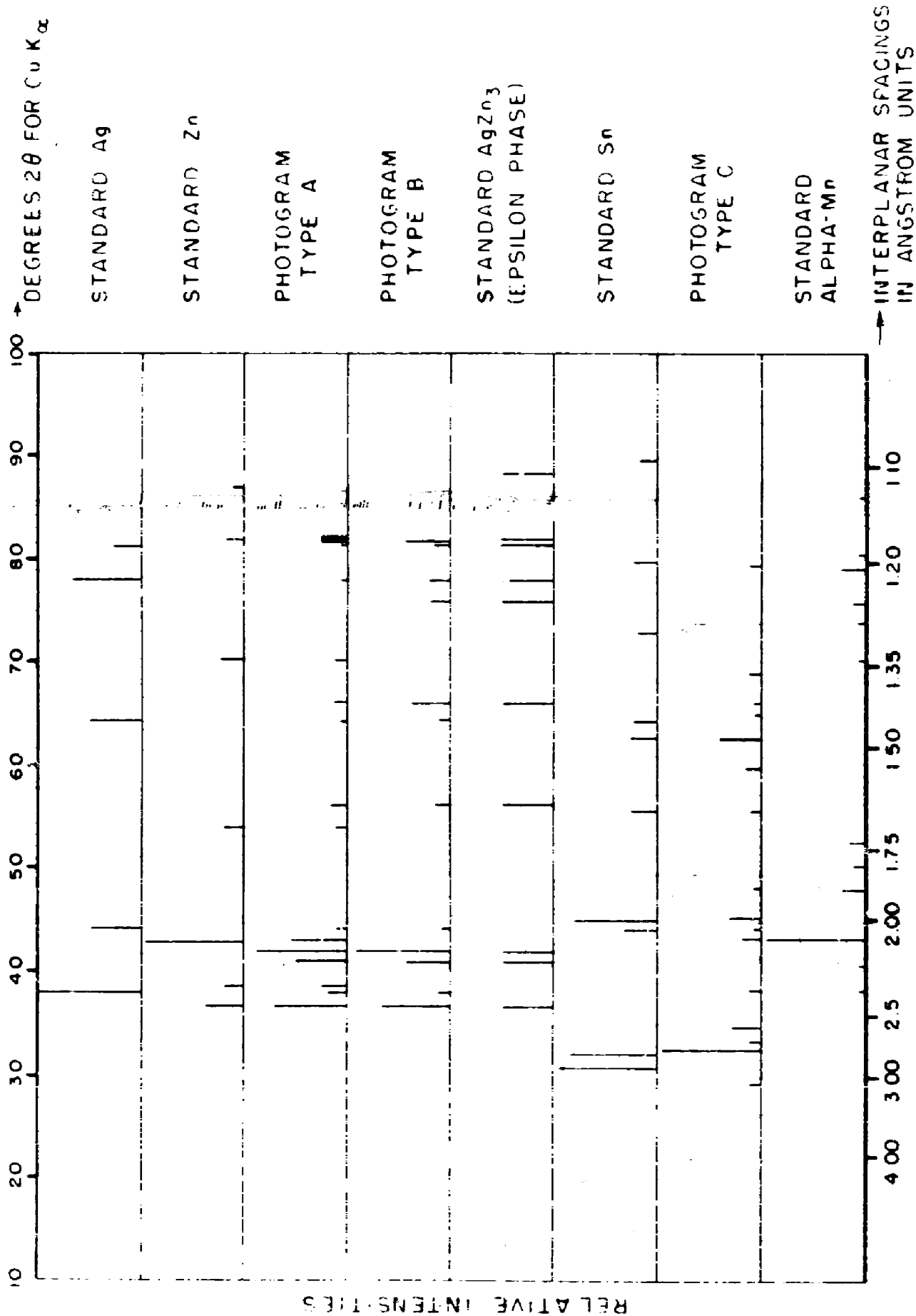


FIGURE 8. GRAPHICAL REPRESENTATION OF X-RAY DIFFRACTION DATA OF TYPICAL SAMPLES EXAMINED WITH STANDARDS FOR COMPARISON.

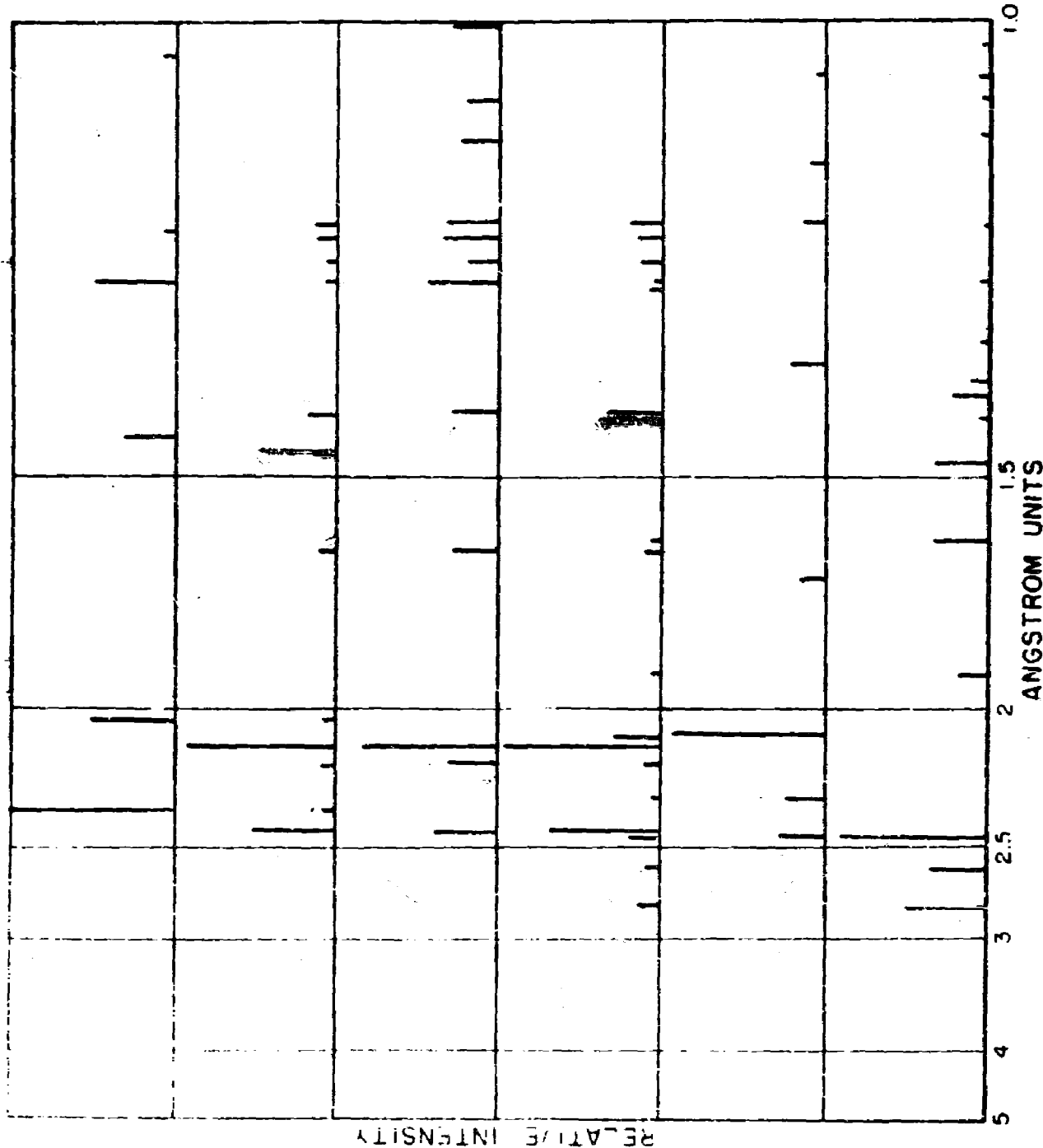


FIGURE 9. GRAPHICAL REPRESENTATION OF X-RAY DIFFRACTION DATA SHOWING THE EFFECT OF SHORT AND LONG TIME DIFFUSION OF Ag-Zn ALLOY WITH STANDARD PATTERNS FOR COMPARISON.

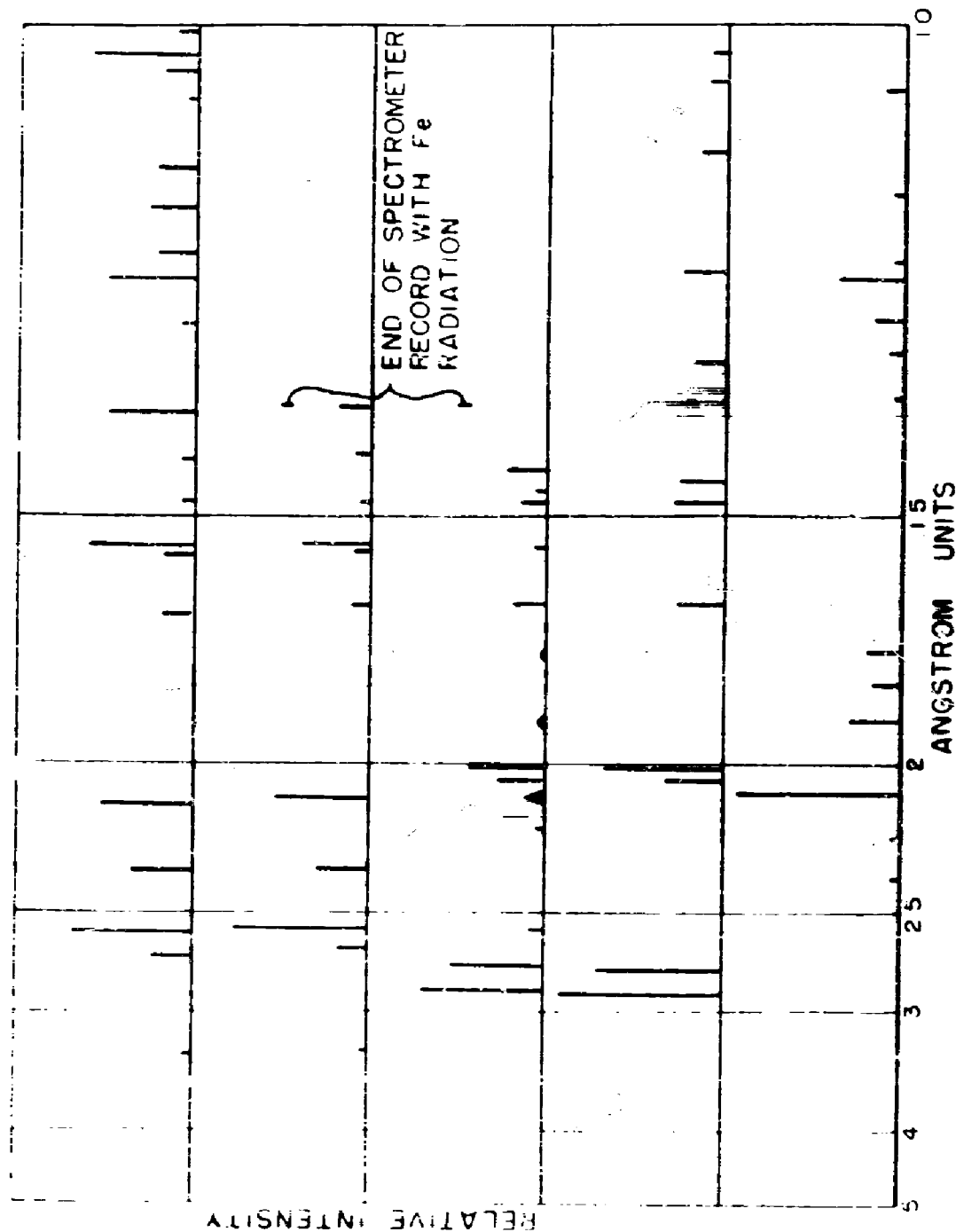


FIGURE 10. GRAPHICAL REPRESENTATION OF X-RAY DIFFRACTION DATA SHOWING THE CHANGE IN STRUCTURE OF Mn-Sn DIFFUSION ALLOY ON AGING AT ROOM TEMPERATURE. STANDARD PATTERNS ARE SHOWN FOR COMPARISON PURPOSES

TABLE 28. POTENTIAL-TIME DATA FOR SEVERAL DIFFUSION ALLOYS IN THREE PER CENT SODIUM CHLORIDE SOLUTION AT 90°F. SATURATED-CALOMEL SOLID. VALUES IN VOLTS.

Specimen Number	Volts* at Elapsed Time of:						
	1 Min.	30 Min.	60 Min.	120 Min.	150 Min.	180 Min.	360 Min.
4557-72B Zn-Ag (diffused) approx. 25% Ag	1.020	1.038	1.043	1.047	-	1.049	1.050
4557-76A(1) Cd-Sn(diffused)	-	0.740	0.747	0.753	-	0.755	0.756
4557-76B(2) Cd-Sn (codeposited,	0.729	0.71	0.728	0.732	-	0.733	0.730
4557-84A Mn-Sn(diffused)	1.02	1.035	1.020	1.032	1.114	1.133	-
2875-72B SAE 4130 steel	0.590	0.710	0.707	-	0.707	-	-

* All values are negative.

- (1) Specimens received from Air Materials Laboratory, Naval Air Materiel Center, Navy Yard, Philadelphia Pa. Composition approximately 50-50.
- (2) Received from same source as 4557-76A. Composition approximately 50-50. Codeposited from fluoride solution.

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